Volume 52 December 1957 Number 8

Economic Geology

and the

Bulletin of the Society of Economic Geologists

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PUBLISHED SEMI-QUARTERLY

Six Dollars Fifty Cents a Year, One Dollar Twenty-five Cents a Copy

THE ECONOMIC GEOLOGY PUBLISHING COMPANY

Printed by Lancaster Press, Inc., Prince and Lemon Streets, Lancaster, Pa.

Entered as second-class matter, March 30, 1906, at the Post Office at Lancaster, Pa., under the Act of Congress of March 3, 1879

Economic Geology

and the

Bulletin of the Society of Economic Geologists

Issued Semi-Quarterly and sent to subscribers on or about the following dates: February 1, March 15, May 1, June 15, August 1, September 15, November 1, December 15.

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Indexed in the Industrial Arts Series.

LANCASTER PRESS, INC., LANCASTER, PA.

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AND THE

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ECONOMIC GEOLOGY

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VOL. 52 DECEMBER, 1957 NO. 8

SULPHIDES IN THE SKAERGAARD INTRUSION, EAST GREENLAND

L. R. WAGER, E. A. VINCENT AND A. A. SMALES
WITH AN APPENDIX BY P. BARTHOLOMÉ

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ABSTRACT

In the chilled marginal gabbro of the Skaergaard intrusion are small specks of chalcopyrite and bornite; the amount of sulphur is .005 percent.

This is taken to be representative of the amount in the 300 km³ of original Skaergaard magma.

In the layered rocks, up to the latest ferrogabbros, sulphides occur in small composite units mostly about 0.4 mm across and forming about .02 percent by weight of the rock. The sulphides are bornite, digenite and chalcopyrite, with some covellite replacing the digenite. In melanocratic bands consisting largely of the heavier crystal fractions, copper sulphides are ten times as abundant as in average rock. It is concluded that immiscible droplets of dominantly copper sulphide liquid formed in the silicate liquid at this stage and could accumulate, as a result of gravity, along with the heavy, primary precipitate silicate and oxide minerals.

In the fayalite ferrogabbros at the top of the layered series droplet-shaped patches of pyrrhotite (mostly altered to marcasite) with a little chalcopyrite but no bornite make up about 2 percent of the rock. At this stage in the fractionation an immiscible sulphide liquid, rich in ferrous sulphide, had formed. In the latest rock fraction, the acid granophyre, pyrrhotite or pyrite with a little chalcopyrite is patchily present up to 4 percent by weight of the rock.

The composition of the latest pyrrhotite has been determined and the composition of earlier immiscible copper sulphide and iron sulphide liquids has been indirectly estimated. The copper-rich sulphide liquid apparently began separating from the silicate magma when the amounts of copper and sulphur in the magma were about .02 and .01 percent respectively. This is considered to represent the solubility of the copper sulphide in the ordinary basic magma at the time of formation of the hypersthene olivine gabbros. With the changing composition resulting from further fractionation the solubility of the copper sulphide in silicate magma increased until the amounts at saturation were .05% Cu and .03% S. The iron sulphide matte separated later when the sulphur content of the silicate magma had risen to about .06 percent and the ferrous iron was about 15 percent. The partition of Cu, Ni and Co between silicate and sulphide liquids is roughly determined at various stages of the fractionation.

The Skaergaard sulphides are low in nickel because, by the time an immiscible iron sulphide liquid separated, nickel had been reduced to very low amounts in the magma as a result of its abundant entry into early olivine and pyroxene. Nickel does not enter the copper-rich sulphide liquid so readily as the later iron-rich sulphide liquid. Cobalt is strongly concentrated in the copper-rich liquid and moderately in the iron-rich. The amounts of palladium, indium and gold have also been determined in selected rocks, from which it appears that at low concentrations the ease of entry of these elements with the partial exception of gold into the sulphide liquid is not markedly greater than into the silicate.

It is suggested that nickeliferous iron-rich sulphides such as the disseminated ores of the Bushveld and Insizwa which separated at an early stage in the crystallization of the magma were formed because there was a relatively high initial sulphur content.

INTRODUCTION

THE Skaergaard intrusion is a layered basic complex in which strong crystal fractionation produced a range of rock types from ultrabasic to acid (38). Sulphide minerals occur (39) but they are less conspicuous on the whole than in many ordinary gabbros and dolerites. On a fourth visit to the intrusion in 1953 when interest in the sulphides had already been raised by some earlier observations, only two rock types were found in which sulphides could be

detected in hand specimens. These were the ferrogabbros of the pyrrhotite horizon which contains the sulphide droplets already briefly described (39, p. 180–2) and the acid granophyre, the latest rock fraction in which irregular patches of sulphide, either pyrite or pyrrhotite, a thousand times larger than the largest droplets of the pyrrhotite horizon are scattered sporadically.

Separation of the sulphides for analysis, except for that in the acid granophyre, has so far proved impossible owing to the small size of the units. We have, however, obtained indirect evidence for some features of the sulphide compositions by radioactivation analysis of series of rocks containing the sulphides in markedly different amounts.

The sulphides in the Skaergaard differentiation series are the same as those described by Newhouse (16) for normal igneous rocks but in the case of this layered intrusion the manner of formation of the sulphides during fractional crystallization of the magma to some extent can be understood. The relation of silicate minerals and sulphide seem to preclude later introduction of sulphide material.

THE SEQUENCE AND ORIGIN OF THE CHIEF ROCK TYPES OF THE SKAERGAARD INTRUSION

It has been shown (38; 39, p. 132–6) that the Skaergaard intrusion consisted originally of a pool of basic magma about 300 km³ in volume. During cooling various processes caused marked differentiation, giving rocks that have been grouped as the layered series and the marginal and upper border groups (Fig. 1). The names used for the rock types developed during differentiation, and their spatial relations, are given diagrammatically in Figure 2 together with the position in the sequence of the chief rocks investigated in this paper. Various lines of evidence show that the layered series was formed as a precipitate of discrete crystals, which separated from an overlying liquid and accumulated as a sediment. The precipitate held some liquid in the interstices at the time of its formation and this necessarily had the composition of the magma existing at that particular stage. As cooling progressed the interstitial liquid crystallized to form outer zones of lower melting point solid-solutions around the primary precipitate crystals, or, additional crystal phases such as apatite and quartz. The nature and general composition of the chief crystal phases, including the sulphides, which form the successive layered rocks, are shown in Figure 2.

The layered series is characterized throughout by rhythmic layering due to marked variation in the proportion of the different minerals. Individual layers may show gravity stratification. The rocks chosen for investigation have normally been average material for the particular horizon, so far as could be judged by eye, but in some cases strongly melanocratic or leucocratic bands formed through the selection of material of special specific gravity, have been investigated.

The original Skaergaard magma is believed to have had the composition of the fine-grained chilled marginal gabbro, which is known from three chemical, and four spectrographic analyses (39, Table A). Gradually the initial

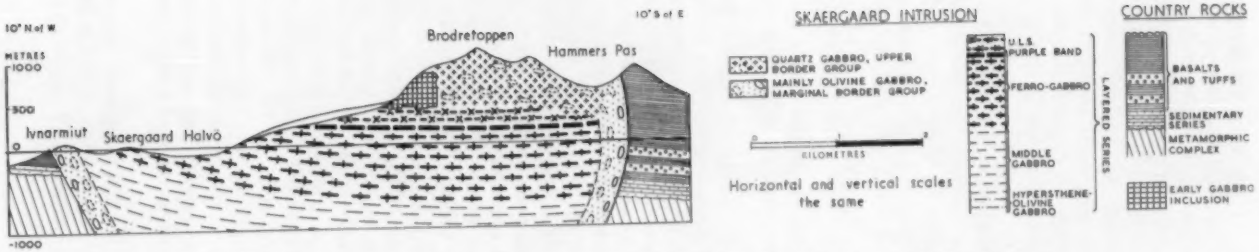


FIG. 1. East-west section across the Skaergaard intrusion showing the principal rock types.

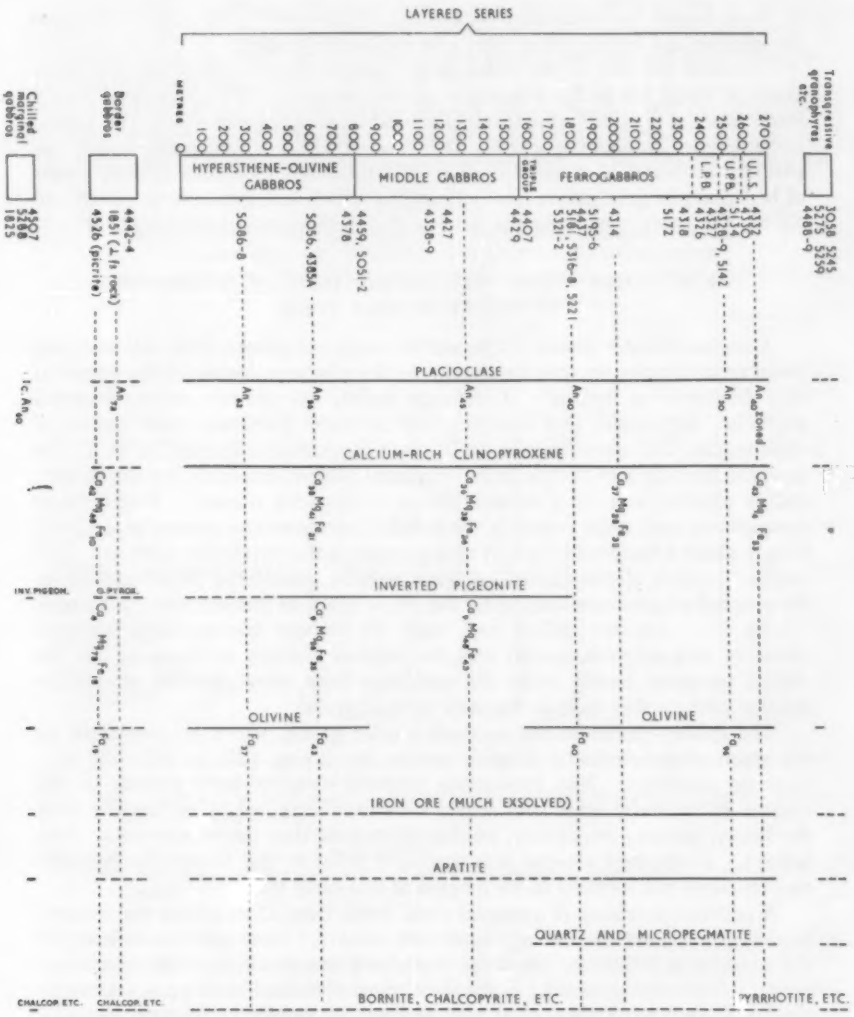


FIG. 2. Minerals present in the various rocks of the Skaergaard intrusion and their compositions. Continuous vertical lines indicate primary precipitate minerals; broken vertical lines are interprecipitate or undifferentiated minerals.

composition of the liquid became modified—slowly at first, then more quickly—by the precipitation of crystal phases of steadily varying composition. Certain arbitrary stages in the successive residual liquids have been defined (38, p. 217). For the major chemical constituents the composition of the liquid

at these stages was estimated previously (38, p. 218–219) and is estimated for sulphur and certain other trace elements in this paper.

Towards the end of the solidification processes there was only a shallow sheet of liquid left in the upper part of the complex. This separated into a lower layer of fayalite ferrogabbro of special type (4139 and 4330) and a basic hedenbergite granophyre (4136, 1905 and 4332). Filter press action apparently occurred at about this stage and produced indefinite sill-like sheets of hedenbergite granophyre and later still, a sill of acid granophyre (3058 and 5275), the latter containing the patches of sulphides of considerable size.

THE SULPHIDES—THEIR TEXTURAL RELATIONS AND DISTRIBUTION IN THE CHIEF ROCK TYPES

Marginal Border Rocks.—The chilled marginal gabbro 4507 collected one meter from the contact with the basalts on the southern margin of the intrusion may be taken as typical. It consists mainly of olivine, augite, inverted pigeonite, labradorite and ilmenite. In polished specimens rare specks of chalcopyrite, and some bornite with exsolved chalcopyrite may be seen. In one case the sulphide occurs within replaced olivine, implying late formation, and in another it is in a minute veinlet cutting the silicates. From rough comparisons with what is seen in the polished specimen the amount of sulphide is only about a hundredth part of that present at the pyrrhotite horizon. The sulphur content of this chilled marginal gabbro, considered representative of the original magma once occupying the whole space of the intrusion, is 55 ppm (Table V). Another chilled rock from the western border, 5288, contains similarly rare sulphide specks and the sulphur content is 60 ppm. In the chilled marginal border rocks the sulphides have no suggestion of definite droplet form as they have in the later layered rocks.

The gabbro-picrite of the northern border group, which is interpreted as the result of accumulation of early olivine by sinking (38, p. 160–64), contains no sulphides. Had immiscible sulphide droplets been present in the magma at this early stage they would have been expected to accumulate with the heavy, primary precipitate, olivine crystals as they do in later rocks (see below). From their absence it is therefore believed that immiscible sulphide droplets were not forming in the magma at this early stage.

A polished specimen of a coarser rock, 4442, from 25 m within the western border group, contains a single moderate sized (.1 mm) patch consisting of chalcopyrite and bornite, the latter containing exsolution lamellae of chalcopyrite. The sulphur present in the rock was determined as 25 ppm, and other similar border rocks have very low contents of sulphur. In none has any concentration of sulphides been found.

Layered Series from 0–2500 m with Copper Sulphides Dominant.—Throughout the lower 2½ km of layered gabbros and ferrogabbros, the sulphides are present in variable amounts and consist of bornite, chalcopyrite, digenite and a little covellite. Some magnetite is closely associated with the sulphides and has clearly a different paragenesis from the bulk of the titaniferous magnetite of the rocks. The sulphide patches are composite or globular.

The common maximum diameter of the larger patches of sulphides is 0.2 mm and the amount of sulphide in the rocks estimated micrometrically on polished surfaces is of the order of 0.02 percent by weight and has not been found to exceed 0.5 percent.

Sulphides in the lower ferrogabbros (1,600–1,950 m) will be considered first. Melanocratic ferrogabbro layers such as 5196 and 4437 (Figs. 3, 5) contain sulphide patches in exceptional abundance. The patches consist of

TABLE I

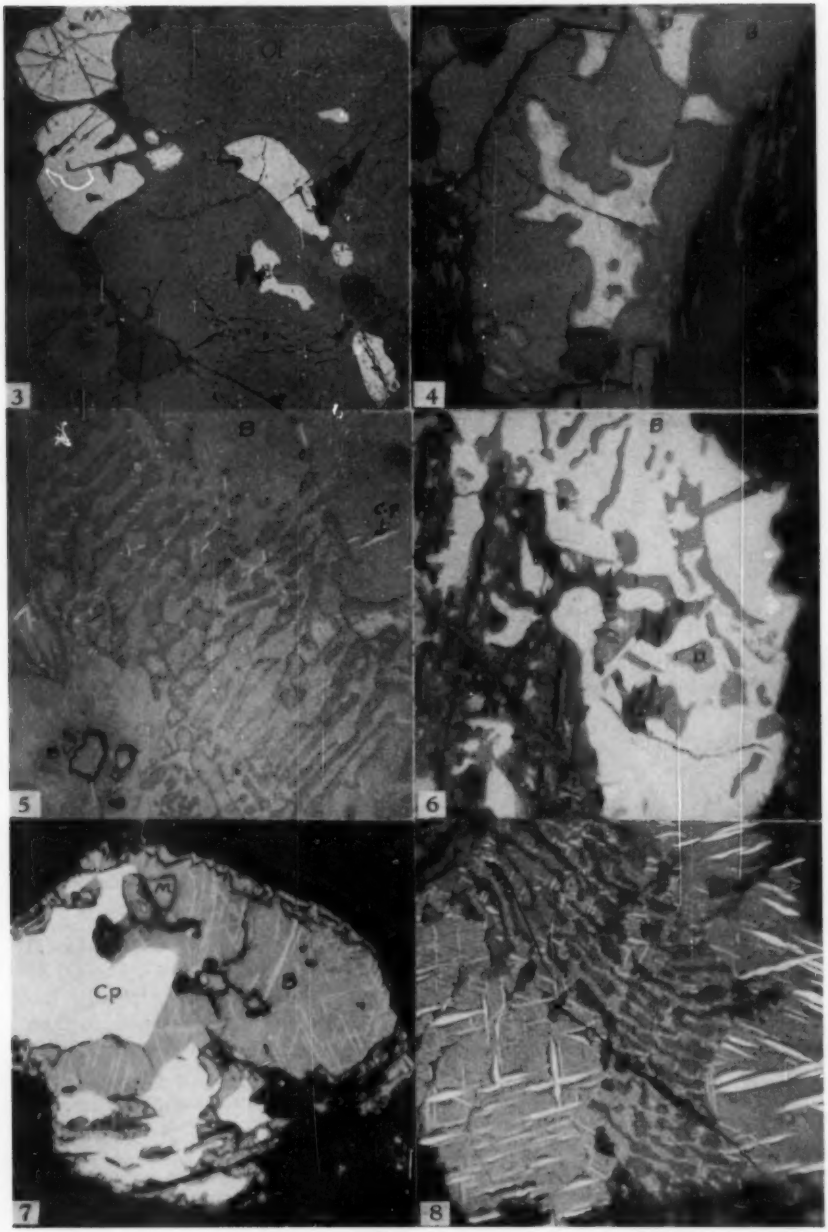
MODES (WT.%) OF FERROGABBROS OF THE COPPER SULPHIDE AND IRON SULPHIDE HORIZONS, TOGETHER WITH SULPHUR DDETERMINATIONS

	Hortonolite ferrogabbros				Fayalite ferrogabbros
	Aver.	Melano.	Melano.	Aver.	
Specimen number	5181	5195	5196	5197	4142 & 4328
Height in meters	1,800	1,899.8	1,900	1,902	2,505
Plagioclase	54	12	16	49	18
Olivine	13	60	31	12	24
Pyroxene	23	3	0	28	36
Iron ore	10	21	39	5	13
Apatite	tr.	4	14	5	3
Quartz or micropegmatite	1	tr.	tr.	1.2	4
Bornite	.027	.40	.42	c. .03	—
Pyrrhotite and marcasite replacing it					2
Chalcopyrite					.15
S by analysis (%)	.016	n.d.	.090	n.d.	.52
Bornite or pyrrhotite equivalents of S	.06 Bornite		.35 Bornite		1.5 Pyrrhotite

5181. Hortonolite ferrogabbro (average rock) 10 yds N.W. of Trough Band G and 30 yds E. of Main House, Skaergaard Halvo.
5195. Lower part of 18 in. band of melanocratic ferrogabbro, west side of small bay 500 yds S.S.W. of Main House.
5196. Melanocratic band 6 in. above 5195.
5197. Average ferrogabbro 5 ft above 5195.
4142 and 4328. Fayalite ferrogabbro of Upper Purple Band, Basistoppen, ½ mile due west of summit.

bornite and digenite.[1] In the case of 5196, measurements of the modal amounts of the sulphide on two different polished specimens gave 0.5 and 0.34 percent (average 0.42%) by weight, Table I. The amount of sulphur in the rocks determined chemically is 900 ppm, which would correspond to 0.35 percent of bornite; the fact that this figure is close to the micrometrically de-

[1] We were uncertain at first whether this mineral was digenite or blue chalcocite. Professor P. Ramdohr, who kindly examined this and other of the sulphides, was also not prepared to decide between these two alternatives in the polished specimen. A small amount of the sulphides, however, was drilled out of the polished specimen by means of a diamond pointed drill (diamond presented by Van Moppes & Son, Ltd.) and powder X-ray photographs obtained which, although confused by lines from impurities, make it clear that the mineral is Digenite and not chalcocite. The term digenite is synonymous with Ramdohr's neodigenite.



FIGS. 3–8.

termined value indicates that essentially all the sulphur is present in the observed bornite and digenite. Another, more average rock, 5181, of about the same horizon had 0.027 percent sulphides from micrometric analyses. The sulphur content was determined as 160 ppm corresponding to 0.06 percent of bornite (Table I).

In the rocks of this horizon bornite and digenite have a patchy relationship (Fig. 4) or form an intergrowth (Figs. 5, 6). The digenite is variable in intensity of color and some has the almost white color of chalcocite. In other cases there is a darker blue material at the contact between the bornite and digenite (Fig. 4).

Chalcopyrite has been found in a few cases as a relatively abundant constituent of the sulphide patches. In one rock, 5221 at 1,800 m, chalcopyrite is about half as abundant as bornite and is in large compact crystals as well as in exsolution lamellae in the bornite (Fig. 7). Chalcopyrite as acicular or lamellar crystals exsolved from the bornite along different directions is not uncommon. It is conspicuous in the sulphides of 5221 which also contain the compact chalcopyrite (Fig. 6); it is seen as occasional needles in the already mentioned rock 4437 (Fig. 5) and it is well seen in some of the rarer sulphide patches lower in the layered series than the rocks at present under discussion (Fig. 8). A felt of abundant chalcopyrite needles is also found in some of the bornite e.g. 5318 at 1,800 m. The acicular crystals from the rather similar felt-like material in the bornite of 4407 at 1,600 m have a strong anisotropy and are believed to be cubanite. The chalcopyrite as lamellae in the bornite is certainly the result of exsolution. The larger compact masses of chalcopyrite 5221 (Fig. 7) were at first regarded as a primary crystallization from a sulphide melt, but Schwartz (25, p. 195) has shown that chalcopyrite in large grains can separate by exsolution from high temperature

FIG. 3. Globules of bornite and digenite (dark gray) among large grains of olivine (Ol), magnetite (M), and apatite. Melanocratic ferrogabbro band 5196 at 1,900 m, Skaergaard Halvö. × 30.

FIG. 4. Sulphide patch of bornite (B) and digenite (D) rimmed by a deeper blue intermediate product. Magnetite (M) partly borders the sulphide. A rosette of an unknown mineral is conspicuous. Average hortonolite ferrogabbro 5181A at 1,800 m near Main House, Skaergaard region. × 330.

FIG. 5. Part of a sulphide patch consisting of bornite (B) with graphic intergrowth of digenite (dark gray) and sporadic exsolved needles of chalcopyrite (Cp). A cluster of magnetite crystals occurs in lower left. Melanocratic ferrogabbro 4437 at 1,800 m, Pukugaqryggen. × 330.

FIG. 6. Part of sulphide patch showing bornite (B) with graphic intergrowth of digenite (D) secondarily altering to covellite (Cv) in which cleavage cracks are conspicuous. Melanocratic ferrogabbro 5318 of the Trough Banding horizon at 1,800 m. × 330.

FIG. 7. Globular patch of compact chalcopyrite (Cp) and bornite (B) with some magnetite (M) and silicate (? hornblende). The bornite shows exsolved chalcopyrite lamellae. Magnetite occurs as a rim to the sulphide or as idiomorphic crystals within it. Ferrogabbro 5221 from the Trough Banding horizon at 1,800 m, ¼ mile NNE of the Main House. × 185.

FIG. 8. Sulphide patch from the Middle Gabbro 4429 at 1,550 m on Pukugaqryggen (melanocratic part of the upper unit of the Triple Group). Bornite (gray) with exsolution lamellae of chalcopyrite, bordered by digenite. A zone across the middle has more extensive exsolution of digenite, which is partly altering to covellite. × 440.

bornite, and investigations of part of the thermal system Cu-Fe-S by Greig, Jensen and Merwin (1, p. 129–34) makes it clear that chalcopyrite of this habit could equally well be the result of subsolidus separation into discrete crystals of chalcopyrite and bornite (see appendix). The exsolution of chalcopyrite as plates in bornite is in some cases accompanied by the formation of digenite along the edges of the chalcopyrite lamellae (e.g. 4429, Fig. 8), an assemblage commented upon in the appendix.

Covellite is found as an alteration product of the digenite in most of the copper sulphide patches; the amount varies from a trace to almost complete replacement. An intergrowth of digenite in bornite is well seen in 5318 (Fig. 6) and this has been about half converted to covellite in which contraction cracks are conspicuous. Some of the covellite is the "blaubleiblendes" variety of Ramdohr (20, p. 523) but some of the ordinary type is also generally present.

Magnetite is seen with an especial relation to the sulphides in most of the sulphide patches. It tends to occur along the borders of the sulphide units and to project into the bornite in well shaped crystals (Fig 4). More rarely it occurs within the sulphide, either showing its own shape (Figs. 5, 7) or as blebby intergrowth within the sulphide. The magnetite of the sulphide patch is free from exsolved ilmenite lamellae and thus is different from the abundant magnetite of the rock away from the sulphide patches (32).

Small amounts of silicate may occur within the sulphide areas and are seen for instance in idiomorphic crystals in Figure 7. From evidence obtained from a large patch of sulphide material, it seems likely that some, at any rate, of the silicate is hornblende.

The sulphides so far described are from the ferrogabbros, at and just above the so-called Trough Banding horizon, 1,800–1,900 m. In rocks above this horizon up to 2,350 m difficulties have been encountered because of weathering, which at first was not realized. The much analysed rock 4318 at 2,350 m (Table V) is now recognized as to some extent weathered. The polished specimen shows only one large sulphide patch, 0.7 mm across in the 4 sq cm of surface. The sulphides are bornite showing a felt of anisotropic exsolution lamellae, probably cubanite as in 4407 described above, and digenite partly altered to covellite. The sulphur content of this rock is 30 ppm (Table V) which confirms that sulphides have not been overlooked in the polished specimen; the low value is however, considered due to weathering which removed the sulphur.

The only rock of about this horizon available, which is apparently unweathered, is 5172 at 2,250 m. In this sulphide patches are sporadic but rather large, and the total sulphide is considerable. The sulphide consists mainly of bornite with a mat of exsolved lamellae. Compact chalcopyrite crystals are also occasionally seen associated with the bornite. Narrow alteration along the margin or cracks giving digenite and covellite has occurred in places. It is believed that this rock must have a sulphur figure of the order of 150 ppm and that this was perhaps the figure for sulphur in 4318 before weathering.

Rocks of the Lower Purple Band around 2,400 m in the layered series are

also low in sulphide. The four rocks that have been particularly examined, 4326, 4327, 4472 and 5276 all have pyroxene in small grains due to inversion from an iron wollastonite. Sulphides are present only in small, ragged specks and consist of chalcopyrite and bornite in about equal amounts, with a little digenite and covellite. One rock, 4327, at 2,455 m has been analyzed; the sulphur content is 40 ppm and copper is 711 ppm. Two other rocks, 4472 and 5276 have been analyzed for copper and gave 460 and 660 ppm respectively. Unfortunately 4327 is weathered and the low sulphur might be due to this. The other two seem unweathered and judged by the abundance of visible sulphides in polished specimens, the amount of sulphur is probably low. Further work on these rocks will be needed to decide whether the copper is present as sulphide or not.

In the lowest exposed part of the layered series, the hypersthene olivine gabbro (0–750 m), sulphide patches of the same general composition and size have been found in some of the rocks examined, but are absent in others. Thus a polished specimen of average rock 5086 at the lowest accessible level showed no sulphide, but a specimen of a melanocratic band 5088 at this same level had one complex mass, 0.14 mm across, containing spongy magnetite, bornite, digenite and a little compact chalcopyrite. Another showed chalcopyrite and bornite with exsolved chalcopyrite. Sulphides have been seen occasionally in other rocks, e.g. in average rock 5056 and melanocratic rock 4378, but no sulphide was seen in average rocks 4459 or 5052. In the melanocratic rock 5051 a trace of native copper and chalcocite was found within the magnetite, but none of the usual copper sulphides were found.

In the Middle Gabbros, 750–1600 in the layered series, sulphides are also sporadic, but seem a little more abundant than in the rocks below. Average rock 4427, and two rocks from the base of the upper unit of the Triple Group 4429 (Fig. 8) and 4407, have a few sulphide patches of moderate size and the usual mineralogy, except that the exsolution lamellae in the bornite of 4407 have strong anisotropy and are thought to be cubanite; average rock 4408, ore-rich band 4358, and ore- and pyroxene-rich 4359 from the Middle Gabbros showed no obvious sulphide and are unweathered; a rock of the Triple Group, 4426, with malachite showing along joints, has cavities believed to result from the removal of sulphides by weathering.

Based on our limited sampling the occurrence of sulphides in these lower layered rocks is sporadic. It was at first thought that sulphides were confined to the melanocratic bands but some were found in average rock, and some ore-rich bands apparently contain no sulphide. The sulphur content of both an average rock (5086) and a melanocratic rock 5088 from 300 m in the layered series is 50 ppm, and the sulphur content of an average Middle Gabbro 4427 from 1200 m is 40 ppm (Table V).

Distributional Evidence for the Existence of an Immiscible Sulphide Liquid.—The high concentration of sulphides in certain melanocratic bands such as 5196 and 4437 compared with the more ordinary rocks must be due to a gravity effect similar to that which produced the concentration of heavy, primary precipitate silicate and oxide minerals in the melanocratic bands. In order that gravity sorting should affect the sulphides as well as the silicates it

is necessary that the sulphides should exist as discrete units. From what is known of the temperatures of crystallization of copper sulphide minerals by Merwin and Lombard (14), and Greig, Jensen and Merwin (1), it is clear that at the temperatures of formation of the primary precipitate silicates, the sulphide would still be liquid and therefore that the sulphide units which collected together with the heavy crystal phases of the melanocratic bands, must have been immiscible liquid droplets. The copper sulphide masses commonly have the form of droplets and have a primary heterogeneity, the result of the crystallization of sulphide-rich liquid into magnetite, silicate, and sulphide. A few minute veinlets of bornite with exsolved chalcopyrite are seen to extend from a sulphide patch through the silicate minerals, indicating the presence of molten sulphide after the rock had largely crystallized. The view that immiscible droplets of sulphide-rich liquid may form in silicate magma is an old one. Vogt in various classic researches (3, p. 278–301; 34) gave good evidence from field occurrence and microscopic textures supplemented by evidence from metallurgical practice and his own experiments. In the case of a layered intrusion produced by bottom accumulation where sorting by gravity is strongly marked, there is conclusive evidence of discrete sulphide-rich units accumulating with the other heavy phases, which at the high temperature of formation of the primary precipitate must have been liquid. At the iron sulphide horizon described below, there is also good evidence from textures of immiscible sulphide droplets having formed in the silicate liquid.

Fayalite Ferrogabbros of the Upper Purple Band with Iron Sulphides Dominant.—At an estimated height of 2,500 m the rusty-purple color of the rocks reaches maximum intensity, and pyrrhotite, or marcasite replacing it, is present to the extent of 1 or 2 percent. The Purple Band of the original paper (38, p. 108) included all the rocks showing evidence of former iron wollastonite; it is now divided into a lower part from about 2,350–2,500 m just described, and an upper, dominantly iron sulphide horizon from 2,500 m to about 2,600 m. The sulphides in the upper Purple Band have been briefly described and figured already from specimen 4142 (39, p. 180–2, 190–2) and further examination and analytical work now enables us to give more details. During the latest visit to the region in 1953 search was made for more extensive sulphide segregations or veins but none were found.

Several polished specimens of fayalite ferrogabbro 4328 of the upper Purple Band, roughly equivalent to 4142 described previously, have been examined. The larger sulphide droplets are 0.25 to 0.3 mm across and are thus much smaller than the plagioclase, pyroxene, and olivine crystals (Fig. 9). In most of the sulphide patches one or two idiomorphic crystals of chalcopyrite are seen and a few magnetite and acicular silicate crystals (Fig. 10), but the bulk of the material is an easily tarnished, spongy, yellow sulphide showing concentric zones of varying sponginess and resistance to tarnishing. Rarely in this rock, and quite commonly in 5134 from nearby, the central parts of the sulphide areas consist of pyrrhotite (Fig. 11). Uniform extinction over the whole, or considerable parts of the pyrrhotite masses shows that the crystal units are large, as is also indicated by the parallelism of the cracks developed during alteration. The spongy-textured sulphide has clearly formed

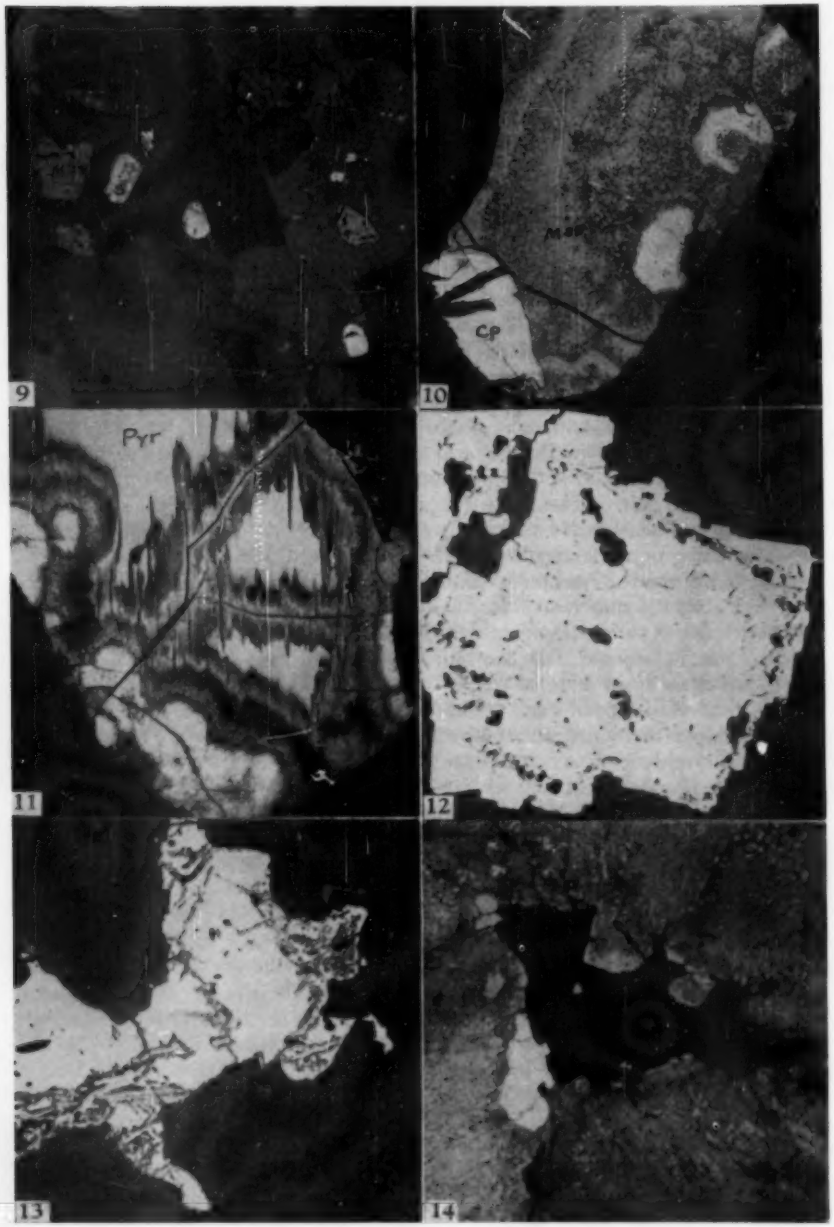
from the pyrrhotite, the alteration taking place from the cracks or from various centers round the margin of the patch. In some zones the replacing sulphide is compact but in others, especially on the fringes of the concentric arcs, it is so porous that it grinds away during polishing. The spongy yellow sulphide is not easy to investigate optically but it is apparently anisotropic, and markedly harder when scratched with a needle than either the chalcopyrite or pyrrhotite. It is also non-magnetic in comparison with the pyrrhotite. Using a minute diamond pointed drill, enough of the spongy sulphide has been obtained to allow X-ray powder photographs to be taken, which prove it to be marcasite. It has been observed in our material that small sulphide patches completely embedded in magnetite remain as pyrrhotite while the patches in the silicates are altered. In some sulphide patches there are minute specks of some different mineral that set up an intense iridescent zone of alteration around them within a few hours of polishing, but the nature of the material has not been determined.

A modal estimate of the sulphides in 4328 is given in Table I (last column); pyrrhotite, and marcasite replacing it, amounts to about 2.0 percent by weight, and chalcopyrite 0.15 percent by weight. The amount of sulphur, determined chemically, is 0.52 percent. If all this were in pyrrhotite (FeS) the amount in the rock would be 1.5 percent. Perhaps this limited agreement is all that can be expected as the sulphide areas are porous in varying degrees.

A nearby upper ferrogabbro 4329 which is estimated as 5 m structurally above 4328 carries essentially similar droplets, of slightly greater size, the larger being 0.4 mm to 0.5 mm across. The sulphur content of the rock, 0.43 percent, is rather less than that of 4328. The previously described 4142 (39, Table 12) is essentially the same as 4328 and has 0.41% S.

Two other upper ferrogabbros were collected 500 m to the SE of 4328 and 4329, near Basistoppen Pass. The lower, 5142 (estimated as at 2,500 m), has much pyrrhotite not replaced by marcasite, and the higher 5134 (2,570 m) shows very clearly an arrested stage of the pyrrhotite replacement (Fig. 11). Professor Ramdohr has pointed out that between the spongy marcasite and the original pyrrhotite there is a typical development of what he calls "Zwischenprodukt" ("Erzmineralien," Figs. 373–376a). Some replacement of pyrrhotite by marcasite has taken place in what seems to be entirely unweathered rock.

The rounded form of many of the pyrrhotite or altered pyrrhotite patches suggests original, immiscible droplets of sulphide liquid. Some of more irregular shapes are presumably due to the effect of the growth of the neighboring silicate or iron-ore crystals. Some sulphide also occurs in ragged, small pieces that we interpret as immiscible sulphide that had not sufficient time to coagulate into bigger droplets. The rather constant average size of the larger droplets in 4328 indicates relatively steady conditions of accumulation and the slightly larger droplets of 4329 slightly different but steady conditions. The form and composite nature of the sulphide patches suggest that they crystallized from an immiscible sulphide liquid consisting mainly of iron sulphide with small amounts of copper sulphide, iron oxide, and silicate. The immiscible sulphide liquid has crystallized to give first the small amounts of



FIGS. 9–14.

magnetite and silicate and then pyrrhotite with a little chalcopyrite. The extensive conversion of pyrrhotite to marcasite does not seem related to weathering and we consider that it took place at a later stage of the cooling of the rock. From the spongy texture of the marcasite, considered to be due to a reduction in volume, it is suggested that the conversion of the pyrrhotite to marcasite took place by elimination of some iron, sulphur remaining constant.

Unlaminated Layered Series and Early Transgressive Granophyres.—After the formation of the fayalite ferrogabbros of the Purple Band, differentiation produced intermediate rocks, previously described as fayalite ferrogabbros, and basic hedenbergite granophyres of the unlaminated layered series (38, p. 42–5). Three of these rocks which have been examined as polished specimens, 4331, 4332 and 4334, show various sulphides, but present in much smaller amounts than in the upper Purple Band. It may be that the sulphides of the upper Purple Band settled out of the magma which ultimately formed the unlaminated layered rocks. In 4330 the sulphide is largely pyrite with a little chalcopyrite: considerable amounts of the semi-opaque secondary ilvaite are present in the rock, though not particularly associated with the sulphides. In 4331 the few small specks of sulphide are mainly pyrrhotite, with a little chalcopyrite. In 4332 the "basic hedenbergite granophyre" there are specks of yellow sulphides with again considerable amounts of ilvaite and the rock does not appear to be weathered. The amount of sulphur in two of these rocks has been determined; in 4330 it is 0.028 percent; in 4332, 0.012 percent. Since the sulphides are very sporadic it was not considered possible to estimate them micrometrically for comparison with the amount of sulphur found by analysis.

Certain granophyres related to, but later than, the rocks just described were originally separated as the transgressive hedenbergite granophyres of Tinden (38, p. 209–13). Two examples (4488, 4489) examined as polished specimens have very little sulphide, and this is apparently pyrite. Much ilvaite is again to be seen widely scattered through the rock.

FIG. 9. Iron sulphide (S) in droplet form in ferrogabbro 4328 (2,500 m) of the Upper Purple Band on west face of Basistoppen. Three complex units of sulphide are embedded in larger crystals of felspars and pyroxene. Some independent magnetite (M) crystallized from the silicate magma is also conspicuous. × 30.

FIG. 10. Enlargement of sulphide patch S of Figure 9 showing chalcopyrite (Cp) with two acicular crystals of transparent mineral (probably hornblende), magnetite around part of the margin and the rest marcasite (Mar.) with a concentric spongy appearance.

FIG. 11. Part of a sulphide patch in the Upper Purple Band 5134 (2,570 m) showing pyrrhotite (Pyr) partly replaced by marcasite. Some of the marcasite has a concentric arrangement; other marcasite, developing from cracks, has a form related to incipient cleavage in the pyrrhotite. × 315.

FIG. 12. Pyrite in acid granophyre 5245 of the transgressive sill on Tinden. The form of the pyrite is due to parallel growth and the crystals are embedded in a granophyric intergrowth of quartz and felspar. × 35.

FIG. 13. Pyrrhotite (white) in acid granophyre 5275A from another part of the transgressive Tinden sill. The pyrrhotite shows some alteration to marcasite along cracks. × 35.

FIG. 14. Thin section in transmitted light of the same acid granophyre as illustrated in reflected light in Figure 13. Well-shaped quartz-felspar intergrowths project into the pyrrhotite (dark area). × 28.

An interesting "basic hedenbergite granophyre" 4334 was found as a loose block. It contained a mass of bornite a centimeter across. The bornite has exsolved chalcopyrite and has altered to two varieties of digenite and some of this has further changed to covellite. Acicular silicate enclosed in the bornite can be seen in a thin section of the rock to be a green hornblende. The rock resembles in general composition the hedenbergite granophyre, but it differs from the other examined in having bornite and not iron sulphides and chalcopyrite; it suggests that a horizon with another association of sulphides remains to be found.

Transgressive Acid Granophyres.—The latest rock of the complex, a transgressive acid granophyre sheet (38, p. 204–9) contains sulphides, the easy decomposition of which makes it very difficult to collect fresh material. A specimen, 5245, from within a meter of the top of the sheet contains irregular patches of pyrite up to a centimeter across (Fig. 12) and probably amounting to about 3% by weight of the rock. The pyrite shows cubic crystal form against the micropegmatite and seems to have crystallized before or simultaneously with the quartz-felspar eutectic. A few grains of chalcopyrite occur in or adjacent to the pyrite.

Another specimen of the acid granophyre of the sill, found in position on the west ridge of Tinden overlooking Brothers Glacier, and similar material collected as a boulder on the beach beneath the sheet, 5275, contains pyrrhotite and not pyrite. The pyrrhotite is in irregular masses of much the same size as the pyrite of 5245 but without crystal form (Fig. 13). Micropegmatitic quartz and orthoclase units of the groundmass have grown in to the sulphide while it was still liquid (Fig. 14). An estimate of the modal amount from a surface of 50 cm^2 gave 3.4 percent by weight of pyrrhotite. A little chalcopyrite occurs as discrete grains in association with the pyrrhotite, just as is the case with the pyrite in granophyre 5245. A rough modal estimate gives the percentage of chalcopyrite to total sulphide as 0.01 percent. Some alteration has taken place along irregular veins in the pyrrhotite, producing anisotropic, parallel lamellae of marcasite at right angles to the cracks.

The pyrrhotite from 5275 was separated and analyzed chemically for Fe, S, Mn, As and by radioactivation for Ni, Co, Cu, Pd and Au (Table II). A slight amount of chalcopyrite equivalent to 0.005% Cu may have been present in the material analyzed and thus about a third of the copper shown by analysis may not be in the pyrrhotite structure. The proportions of iron and sulphur are not greatly dissimilar from that of the pyrrhotite in the basic rocks of Insizwa (24, p. 154), but the amount of Ni is of a very different order.

The acid granophyre sill was formed from a late acid magma produced by filter-press fractionation from the Skaergaard magma approximately in the position it now occupies, and it must have cooled slowly as the whole complex cooled. No considerable temperature difference at any time between one part of the sill and another can reasonably be postulated. It is thus surprising that the sulphide is pyrrhotite in one place and pyrite in another. The pyrite, being in clusters of well-shaped large cubes, which are idiomorphic toward the granophyric material, is believed to have crystallized earlier than the silicates from small masses of sulphide magma which were patchily distributed in the

granophyric magma; the crystallizing pyrite apparently pushed aside the silicate magma while the latter was still liquid (cf. Vogt, 35, p. 644–5). The nature of the contact between the pyrite and the micropegmatite and the isolation of the pyrite crystals seems to preclude replacement as an explanation of the texture. An alternative hypothesis, that pyrite crystallized from sulphide dissolved in the silicate liquid, is not likely because the amount would exceed, by many times, the probable solubility of iron sulphide in acid magma (43, p. 391). Newhouse (16, p. 10) notes that in many of the granites that he examined pyrite was the dominant sulphide and tended to show well shaped

TABLE II

ANALYSIS OF PYRRHOTITE FROM THE ACID GRANOPHYRE OF THE SKAERGAARD INTRUSION AND COMPARISONS

(Ni, Co, Cu, Pd and Au by radioactivation analysis)

	A	I	B	C
Fe[2]	63.53	61.75	60.4	58.22
S[2]	36.47	37.53	38.1	41.78
Mn[2]		0.03		
As[2]		0.005		
Ni[1]		.0001	.3[5]	
Co[1]		.0232		
Cu[1]		.0149[4]	1.1[5]	
Pd[3]		.000001		
Au[3]		.0000003		
Loss at 110°C		.34		
Insoluble in acid		.49		
		100.18		
Formula	FeS	$Fe_{0.94}S_1$		$Fe_{0.9}S_1$

A. FeS (theoretical).

I. Pyrrhotite from acid granophyre 5275, Skaergaard Intrusion, Anal. E. A. V. & A. A. S. and J. H. Crocket.

B. Pyrrhotite, Insizwa Mountain, Griqualand, South Africa (24, p. 81).

C. $Fe_{0.9}S_1$.

[1] Analysis by A. A. S.

[2] Analysis by E. A. V.

[3] Analysis by J. H. Crocket (Unpublished thesis, Oxford University).

[4] Some of the Cu may be from grains of chalcopyrite associated with the pyrrhotite but amount estimated from polished specimen less than .005.

[5] Cu and Ni partly due to chalcopyrite and pentlandite visibly associated with the pyrrhotite.

crystal form. The pyrrhotite of our rocks does not show crystal shape, but has the form of interstitial patches. Felspar and quartz-felspar intergrowth in well shaped crystals are seen in thin section to project into the pyrrhotite (Fig. 14), which must have been liquid at the time of crystallization of these silicates.

Summary of Sulphide Distribution and its Implications.—The general distribution of the sulphides and related minerals in the various rocks of the intrusion is summarized in Table III. Micrometric estimates of the amounts of the sulphides in selected rocks have already been given (Table I).

The chalcopyrite with rare bornite occurring in ragged, small pieces in

the chilled marginal gabbro and outer marginal border rocks, is regarded as having formed locally from the silicate magma. In the original magma, and probably during the early stages of the fractionation corresponding roughly to the time of formation of the hidden layered series, it seems likely that no immiscible sulphide droplets formed in the main body of the magma.

After these early stages immiscible copper-rich sulphide liquid, now bornite, digenite and chalcopyrite, formed in the main body of the magma

TABLE III

SULPHIDES IN THE VARIOUS PARTS OF THE SKAERGAARD INTRUSION

Rock		Structural height in meters	Observed sulphides and related minerals	Average amount in ppm (see also Table V)	
				Sulphur	Copper
Transgressive acid granophyre			Either pyrite in large crystals with trace of chalcopyrite, or pyrrhotite in patches with similar chalcopyrite. Lamellae of secondary marcasite along cracks in pyrrhotite.		140
Basic hedenbergite granophyres		c.2600	Only rare sulphides. In some rocks pyrite; in others pyrrhotite, a little chalcopyrite.		150
Fayalite ferrogabbro	High P.B.	2500–2600	Pyrrhotite droplets with chalcopyrite and magnetite. Pyrrhotite largely replaced by marcasite with concentric spongy texture.	5000	200
	Low P.B.	2350–2500	Only rare specks of sulphides—bornite and chalcopyrite.	40*	700
Ferrogabbro (ferrohortonolite)		1950–2350	Bornite, digenite and chalcopyrite associated with nontitaniferous magnetite. Exsolution lamellae in bornite of chalcopyrite or cubanite. Covellite partly replaces digenite; chalcocite may be present.	30*	850
Ferrogabbro (hortonolite)		1550–1950		160	630
Middle gabbros		750–1550		40	90
Hyperothene olivine gabbros		0–750		50	110
Hidden layered rocks			Probably little sulphide.		
Chilled marginal border and other marginal border gabbro			Rare specks of chalcopyrite and rarer bornite; chalcopyrite exsolution lamellae may be developed in bornite.	50	110

* Low because of weathering.

over a long period of the fractionation. Then at a late stage the dominantly copper sulphide liquid was replaced by a dominantly iron sulphide liquid, now pyrrhotite with a little chalcopyrite, the pyrrhotite being much altered to marcasite. Finally, in the acid granophyre, the latest differentiate, pyrrhotite or pyrite occurs relatively abundantly. The sequence during fractionation is very clearly copper sulphides first and iron sulphides later.

In magmatic ore deposits, such as Namaqualand (11), Engels' mine, Plumas County, Calif. (30, p. 61–4), it has been noted, as in the Skaergaard

intrusion, that bornite and pyrrhotite are antipathetic, but that chalcopyrite or other intermediate copper-iron sulphide may occur with either. A discussion by Dr. P. Bartholomé of the phase relations based on recent experimental data is given in the appendix.

ANALYSIS OF THE SULPHIDE BEARING ROCKS AND ESTIMATES OF THE COMPOSITION OF THE IMMISCIBLE SULPHIDE MAGMA AT VARIOUS STAGES

Analytical determinations of sulphur [2] by colorimetric and gravimetric methods in a series of critical rocks have been carried out by one of us

TABLE IV

SELECTED ANALYSES OF ROCKS ASSOCIATED WITH MAGMATIC SULPHIDES

	I	A	B	C	D	E	F	G
SiO_2	48.07	47.84		50.88	54.64			
Al_2O_3	17.23	16.98		16.85	16.70			
Fe_2O_3	1.47	3.18		1.46	2.09			
FeO	8.99	7.92		8.84	6.89			
MgO	8.78	6.73		7.14	5.00			
CaO	10.94	10.01		10.72	7.11			
Na_2O	2.33	2.63		1.80	2.98			
K_2O	0.30	.48		0.21	1.65			
H_2O^+	0.83	2.23		0.34	1.53			
H_2O^-	0.04	.08		.02				
TiO_2	1.05	1.53		1.24	1.12			
MnO	0.13			0.32	.39			
P_2O_5	0.09	.18		0.13	.16			
S	.0055	.026	.012				.1	.005
Cu	.0126	.012	.040			.016	.025	.011
Ni	.0193	.018				.008		.018
Co	.0056	.0045				.0035		.0055
Pd	.000,0018							
In	.000,0054							
Au	.000,0005							

I Chilled marginal gabbro 4507 (= original magma), 3 ft in from south margin, Skaergaard intrusion. (New analysis by E. A. Vincent and A. A. Smales.)
A Greenstone Flow, Keweenawan, Michigan, U. S. A. weighted average (6, p. 152). Figures for Ni and Co from Sandell and Goldich, 22).
B Fresh "trap," Keweenawan, Michigan, analysis of composite sample (4, p. 45).
C Average two analyses of chilled floor phase of Bushveld Complex (15, p. 53, Anal. A, B).
D Average composition of basic member of Sudbury nickel eruptive, Ontario (17, p. 34).
E Figures for average basic rock at 48% SiO_2 read from graphs (22).
F Selected average figures for basic rock (31).
G Preferred estimate of amounts of certain constituents in the original Skaergaard magma using I and data from Table V.

[2] The usual gravimetric determination of sulphur in rocks as $BaSO_4$ is so inaccurate as to be useless at concentrations below 100–200 ppm, and a colorimetric method for determining traces of S in metals, developed by Luke (13), has been applied to rocks containing up to 100–200 ppm S. The rock powder is decomposed by sintering with Na_2O_2 at 500° C (19, p. 485–91) and the acidified solution distilled with H_3PO_2 and HI under carefully standardised conditions. The H_2S in the distillate is converted to a PbS sol, the transmittancy of which is measured on a spectrophotometer. Alternatively, the H_2S may be converted to Lauth's violet, as described by Polson and Strickland (18). The reproducibility attained by using these methods is not good at low concentrations, the results obtained in replicate determinations varying by factors up to 2.

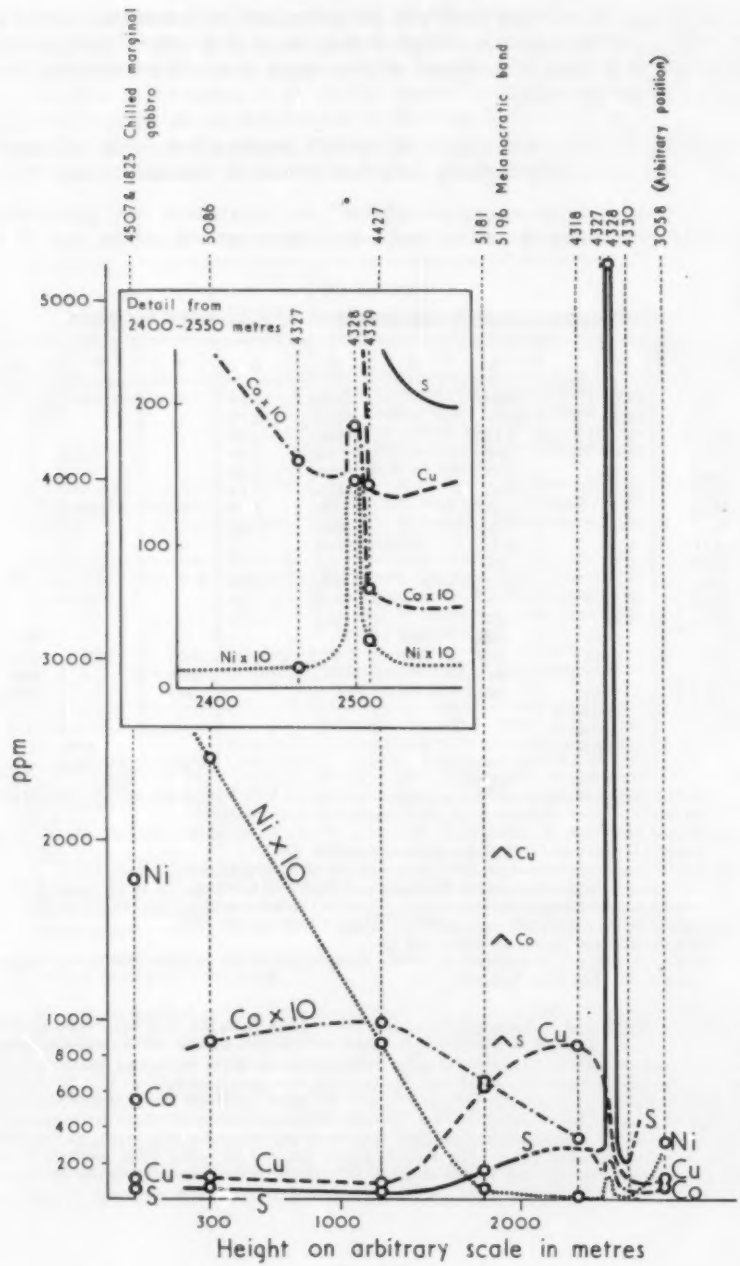

4507 & 1825 Chilled marginal gabbro
5086
4427
5181
5196 Melanocratic band
4318
4327
4328
4330
3058 (Arbitrary position)
Detail from 2400–2550 metres
4327
4328
4329
Co x 10
S
Cu
Co x 10
Ni x 10
Ni x 10
200
100
0
2400
2500
5000
4000
3000
2000
1000
800
600
400
200
ppm
Ni
Ni x 10
Co x 10
Co
Cu
S
Cu
S
S
Cu
Ni
Cu
Co
300
1000
2000
Height on arbitrary scale in metres

FIG. 15.

(E. A. V.). Ni, Co and Cu have been determined by radioactivation analysis (A. A. S.) in certain of the rocks and in the pyrrhotite extracted from the acid granophyre. Details of the methods are given in a separate publication (28). In a few cases gold, palladium (33) and indium (40), have also been determined by radioactivation. It was considered justified to use these highly accurate radioactivation methods to establish the amounts of these elements in the original magma and in certain layered rocks, in order to obtain indirectly an estimate of the composition of the sulphide liquid phase.

S, Cu, Ni, Co, In, Pd and Au in the Original Magma.—The composition of the original magma from which the Skaergaard complex was formed is considered to be represented by the chilled marginal gabbro. A specimen of this rock, 4507, collected one meter in from the southern margin of the intrusion, is now taken as the best example, and has been analyzed (Table IV). In Table V some other analytical data for two other chilled marginal border gabbros (5288, 1825) are also presented and a weighted average composition for S, Cu, Ni, and Co is given in Table IV, last column. In making this average the high nickel in 5288, which is quite definitely shown by the radioactivation results, is considered due to a concentration of early olivine and has been ignored. The low sulphur values in the outer border rocks, 4442, 4443, and 4444 which are successively farther from the margin, may be due to these rocks being formed from early crystal accumulates which were free from sulphide together with the contemporary liquid, the sulphur present being that originally in the interprecipitate liquid. The reason for the low sulphur in 1825 does not seem to be explicable in the same way and suggests that this is not typical.

The amount of sulphur present in the original Skaergaard magma is taken as 0.005 percent (average of that for 4507, 5288, 1825). This is much lower than the amount (0.05%) previously given (39, p. 179). There are probably few determinations of sulphur in undifferentiated basic rock which are satisfactory. Most analyses do not include sulphur and if they do, the reason for its determination is usually that some richness in sulphur was anticipated or that sulphide was actually visible. The average figure of 0.1% S for basic rocks given by Tröger (31) is likely to be totally unrepresentative of average undifferentiated basic magma. Perhaps the best comparative figures (see Table IV) are those for a composite sample of "Fresh trap" from Michigan (4, p. 45) and a weighted average of 17 analyses of the Greenstone Flow, Michigan, by Cornwall (7, p. 152). These averages are between two and five times the amount determined for the Skaergaard magma. It seems that the initial Skaergaard magma was less rich in sulphur than the Keweenawan basaltic magma.

The differences between the amounts of Ni, Co and Cu found in different samples of the chilled marginal rock (Table V) far exceed the precision of the radioactivation method. Taking into account sampling differences, it seems likely that the amount of these elements in the Skaergaard magma is now known to within about ten per cent. It is satisfactory to find that the

FIG. 15. Variation in the amounts of sulphur, copper, cobalt and nickel in average rocks of the intrusion plotted against structural height. (Amount in melanocratic band 5196 shown: ∧.)

previous figures obtained for these elements by optical spectrography (39, Table A) are close to the new values.

The amounts of In, Pd and Au in the chilled marginal gabbro are, as anticipated, very low. The amount for these elements is of the same order as that in the standard dolerite W-1 from Virginia (33, 29).

TABLE V

AMOUNTS IN PPM OF CERTAIN ELEMENTS IN ROCKS OF THE SKAERGAARD INTRUSION—SULPHUR BY CHEMICAL METHODS, THE REST BY RADIOACTIVATION ANALYSIS

Rock	Structural height (meters)	S[2]	Ni[3]	Co[3]	Cu[3]	Pd[3]	In[4]	Au[5]
		Late Rocks						
Acid granophyre 3058		(ca. .1%)	28	6.1	136		.091	.003
		Layered Series						
Basic hedenbergite granophyre 4332	2590	120	3.3	10.5	213			.009
Fayalite ferrogabbro of unlaminated layered series 4330	2590	280	1.5	2.3	63			
Upper P.B. ferrogabbro 4329	2505	4300	3.2	7.0	135			
Upper P.B. ferrogabbro 4328	2500	5200	14	18	318	.019	.18	.003
Lower P.B. ferrogabbro 4327	2455	40*	1.5	16	711		.17	
Ferrogabbro 4318	2320	30*	1.0	34	845			
Melanocratic ferrogabbro 5196	c. 1900	900	4.2	147	1962	.01		.028
Average ferrogabbro 5181	c. 1800	160	4.2	65	626		.079	.003
Middle gabbro 4427	1230	40	86	99	90			.002
Hypersthene-olivine-gabbro 5086	280	50	244	87	112		.060	.03
Hypersthene-olivine-gabbro 5087	280	50						.005
Melanocratic hypersthene-olivine-gabbro 5088	280	50						.005
		Marginal Border Group						
	Distance from margin							
Chilled olivine-gabbro 4507	1	55	193	56	126	.018	.054	.005
Chilled olivine-gabbro 1825	3	25	165	54	97			
Chilled olivine-gabbro 5288	10	60	429	82	100			
Perpendicular felspar rock 1851	20	35						
Coarse olivine-gabbro 4442	25	25						
Coarse olivine-gabbro 4443	70	40						
Coarse olivine-gabbro 4444	210	10						

[1] Averages of 2 to 6 replicate determinations by E. A. Vincent.
[2] Roadiactivation analyses by A. A. Smales.
[3] Radioactivation analyses by E. A. Vincent.
[4] Radioactivation analyses (see Wager, Smit and Irving, 1957).
[5] Radioactivation analyses by J. H. Crocket (Unpublished thesis, Oxford University).
* Low because of weathering.

Variation of Certain Elements in Selected Rocks of the Fractionation Sequence.—The variation of S, Ni, Co, Cu, Pd, In and Au in selected rocks is given in Table V and that part of it referring to average layered rocks is presented graphically in Figure 15, where the amounts are plotted against height in the intrusion.

The general variation of nickel and cobalt in the average layered rocks has been given before, based on spectrographic data (39). The present analyses by radioactivation are more precise and besides showing the general

fall in nickel to very low figures in the ferrogabbro from 2000–2500 m they show a small but significant rise in nickel content in the upper Purple Band (Fig. 15). Since this coincides with the incoming of abundant iron sulphides the increase in nickel is ascribed to the entry of nickel into the sulphide phase. The amount of cobalt in the rocks falls steadily in the upper ferrogabbros except at the iron sulphide horizon, where again the slight increase is ascribed to the sulphide.

The sulphur and copper content of the layered rocks up to about 2,000 m show sympathetic variation, the ratio of the two elements being of the right order to form copper sulphide minerals, and the actual amounts being roughly appropriate to the amounts of sulphide seen in the polished specimen. However, in the rock 4318 at 2,350 m (Table V) the sulphur is only 30 ppm and the copper is 845 ppm. This unexpected behavior of the copper and sulphur had been commented upon before and ascribed to the entry of copper into the silicate minerals (39, p. 179 & 191). This suggestion is not confirmed by the result of further colorimetric analysis of separated minerals from the rock 4318 given in Table VI. The minerals analyzed make up 97 percent of the rock as shown by the results of micrometric analysis. The remaining part of the rock is quartz and orthoclase, chlorite, and hydrated iron oxide, the latter distinguishable as patches and veins in the polished specimens. The contribution of each of the six main minerals to the total copper content of the rock is less then a tenth of the total (third column, Table VI). The copper must, therefore, be present largely in the late crystallizing interstitial materials or in the hydrated iron oxides. To test this, acid extracts were analyzed for copper. Extraction with dilute HCl for 1½ hours, dissolved 21 percent of the sample and the extract contained 3,200 ppm Cu. With HNO_3 17.5 percent of the sample was dissolved and contained 3,700 ppm Cu. The acid dissolved the brown iron oxide and attacked to some extent the olivine and magnetite. The small amounts of copper in the dissolved olivine will make no appreciable contribution to the content of copper in the extract and even the magnetite will make only a small contribution. It is clear that the copper largely exists associated with, or in, the latest crystallizing minerals, including the hydrated iron oxide. The amount of copper in this material is of the order of 6 percent but we have not identified any definite copper mineral. For this rock the explanation of the unusual relative proportions of sulphur and copper seems to be that slight weathering has decomposed the sulphides with the almost complete removal of sulphur and the retention of the copper, probably in with the hydrated ferric oxide.

Rocks of the Lower Purple Band contain high copper and little visible sulphide even when apparently fresh. The question of the mineral in which the copper occurred has not yet been solved for these rocks, which immediately precede the iron sulphide horizon.

In the graphical plot of the sulphur content of the rocks (Fig. 15) the curve is broken from 2,000–2,500 m. The sulphur content of fresh rock is not known owing to the inadequate collecting and the curve is drawn on the assumption that the sulphur amounts, as in the lower series, are proportional to the copper.

Sulphur in the highest layered rocks reaches 0.5 percent, an amount that corresponds reasonably well with the iron sulphides visible in polished specimens (Table I). In the later intermediate and acid rocks sulphides are sporadic and the rocks have not been analyzed for sulphur.

Composition of the Copper-rich Sulphide Liquid.—The curves of Figure 15 are for average rocks as estimated by eye in the field and it is satisfactory to find them so smooth. The figures for the melanocratic band 5196, 100 m higher than the average rock 5181 are also indicated. Sulphur in the melanocratic band is 5½ times that in the average rock; copper is 3 times, cobalt twice, and nickel the same. It is possible from these data, together with previous determinations of the amount of these elements in the dominant minerals at this horizon, to obtain a rough estimate of certain compositional features of the sulphides (Table VII). Thus the amounts of Ni, Co and Cu in the rock due

TABLE VI

COPPER CONTENT OF INDIVIDUAL MINERALS OF FERROGABBRO 4318 AND ESTIMATION OF CONTRIBUTION OF THESE TO THE COPPER CONTENT OF THE ROCK

	Copper* in ppm	Modal amounts of the minerals (wt. %)	Copper in 10^4 gram rock due to the first six minerals
Plagioclase	75	37	28
Olivine	120	17	20
Pyroxene	60	29	17
Magnetite	500	11	30
Ilmenite	130		
Apatite	c. 200	2.3	5
Micropegmatite, goethite, etc.		3.1	
Acid extract (21%) including all the goethite, and some olivine, apatite, and iron ore	3200		
Rock	845		100

* Determined colorimetrically by E. A. V. (method of Sandell, 23), except for apatite which was by spectroscopy (39, Table B), and the rock which was by radioactivation (see Table V).

to the non-sulphide minerals may be estimated from the modal amounts of the minerals and spectrographic data on their composition (39, Table B, column D). By subtracting the amounts in the non-sulphide minerals from the amounts found in the rock, which includes 0.4 percent of sulphide, a rough figure for the percentages of those elements in the sulphide is obtained. The figures for copper and cobalt in the sulphide may no doubt be accepted as of the right order. For nickel the method cannot be used as the amounts are so low that the spectrographic data on the nickel content of the minerals are not precise enough for the present purpose. The sulphide-rich rock, however, contains only the same low amount of Ni as the average rock. This is known with precision and thus it seems certain that Ni cannot be strongly concentrated in the 0.4 percent of copper sulphides. The rock 5196 also differs from 5181 in having a greater amount of olivine and ore which are relatively rich in nickel, compared with felspar. The greater height in the intrusion means that the Ni of the silicates will be slightly lower, while the greater

amount of olivine and ore in the rock will tend to increase the amount of Ni. If the amount of Ni in the 0.4 percent of sulphide was as much as 250 ppm, then the amount of nickel in the rock would be increased by 1 ppm. We consider that if the sulphide had contained this amount of nickel the amount in the rock would have been 5–6 ppm. The radioactivation analysis shows clearly that this is not the case and thus we estimate the nickel content of the sulphide as less than 250 ppm.[2]

An estimate of the overall composition of the copper-rich sulphide liquid as it existed before crystallization may also be made. The crystallized droplets consist largely of bornite and digenite with a little chalcopyrite, together with about ten percent of magnetite and a few percent of silicate. By modifying the percentage composition of bornite by the addition of 10 percent magnetite, 2 percent silicate and by amounts of Co and Ni to give the ratios relative to copper deduced in the preceding paragraph, an estimate may be obtained of the composition of the immiscible sulphide liquid at the early ferrogabbro stage (Table VIII, column I).

TABLE VII

ESTIMATED AMOUNTS OF CERTAIN ELEMENTS IN THE SULPHIDE OF THE MELANOCRATIC FERROGABBRO 5196

	Plag.	Olivine	Pyrox.	Ore	Ap.	Estimated totals in non-sulphide minerals	Amounts found in 10^4 g of rock 5196	Estimated amount in 0.4% sulphide (by subtraction)
Percent of rock	16	31	0	39	14			
Cu	40	90	0	200	30	360	1962	1600
Ni	0	3	0	5	0	8	4.2	
Co	0	30	0	65	0	95	147	50

Notes. 1. Cu, Ni and Co in individual silicate minerals determined spectrographically and in ore and the rock by radioactivation analysis.
2. The amount of Ni in the minerals apparently exceeds that in the rock because of the limited accuracy of the spectrographic data and no estimate of Ni in the sulphide is possible.

Composition of the Iron-rich Sulphide Liquid at the Pyrrhotite Horizon.—Around 2,500 m, where iron sulphide becomes relatively abundant, the sulphur determined chemically is of the order of 0.5 percent (Table V). The crystallized droplets consist of pyrrhotite (or marcasite replacing it), chalcopyrite, a little magnetite (about 2 percent) and a trace of silicate. The ratio of original pyrrhotite to chalcopyrite from modal determination is approximately 13 to 1 (Table I) and this is used in estimating the copper content of the immiscible sulphide liquid (Table VIII). The curves showing the Ni and Co contents

[2] It would have been far more satisfactory to have separated the sulphides and analysed them directly. Attempts were made to drill them out but there was too much contamination from adjacent minerals. Mr. Patching of the Mineral Dressing section of the A.E.R.E., Harwell, offered to try to separate them by flotation methods and Mr. Mueller and Mr. Pownall worked on a small amount of both the rock containing copper sulphide and that containing iron sulphide, but reasonable amounts of sulphide concentrates could not be obtained.

TABLE VIII

PERCENTAGE COMPOSITION OF THE IMMISCIBLE SULPHIDE LIQUID AT VARIOUS STAGES

	I	II	III
S	23	34	38
Fe''	10	61	62
Cu	53	2.3	0.015
Mn	—	—	0.03
Ni	<0.025	.06	.0001
Co	2	.02	.02
Fe_3O_4	10	2	0
Silicate	c. 2	c. 1	0

I Copper sulphide liquid at lower ferrogabbro horizon (estimated).
II Iron sulphide liquid at fayalite ferrogabbro horizon (estimated).
III Iron sulphide liquid at acid granophyre stage (actual analysis).

of the average rocks at different heights in the intrusion (Fig. 15) show an abrupt change of direction when the iron sulphide droplets are found, and it is reasonable to assume that the changes are due to the incoming of the sulphides. The increase of 12 ppm in the nickel content and about 5 ppm in the cobalt content of the rock is considered due to the 2 percent of sulphide in the rock. This means that the sulphide must contain about 600 ppm Ni and 250 ppm Co to have the effect noted on the nickel and cobalt content of the whole rock.

Assuming that the sulphide liquid was generally of pyrrhotite composition with 2 percent magnetite, 0.15 percent chalcopyrite and that the amounts of Ni and Co were as indirectly deduced above, the composition of the sulphide liquid at this stage is roughly as estimated in column II of Table VIII.

Composition of the Latest Sulphide Liquid.—In the latest rock of the complex, the acid granophyre, the sulphides, which are either pyrrhotite or pyrite, are so patchily distributed that a chemical determination of sulphur was not attempted. The sulphide content varies from 4 percent by weight down to a hundredth part of this, and there is evidence of the oxidation and replacement of sulphides in some of the rocks as a result of weathering. The graphs for sulphur (Fig. 15) have therefore not been continued as far as the acid granophyre. Only a rough idea of the solubility of iron sulphide in silicate-rich melts is available but this is sufficient for it to be highly unlikely that the 1 or 2 percent of sulphide in the sulphide-rich granophyres could have been contained in solution in the silicate melt. The development of the acid granophyres has been ascribed to filter press action on the partially solidified later rocks of the complex (38, p. 306). It is now suggested that filter pressing of the crystal mush drove off sulphide liquid as well as silicate liquid. If this is so, the sulphide in the acid granophyre must not be looked upon as separating from the granophyre itself but from earlier magma. The sulphide liquid may, however, have been held in suspension in the silicate liquid long enough for the amounts of minor constituents such as Ni and Co in the two liquids to reach equilibrium. The composition of this latest sulphide liquid is believed to be essentially the same as the pyrrhotite analyzed from this rock (Table II).

Comparisons of the Sulphide Liquid Compositions.—The immiscible sulphide liquid separating during most of the Skaergaard fractionation process was certainly copper-rich; it also apparently contained a moderate amount of cobalt but was clearly low in nickel (Table VIII, column I). It is thus markedly different from the nickeliferous pyrrhotite of the magmatic ore deposits believed to have separated from basic or intermediate rocks. A later sulphide liquid was iron-rich but with some copper (Table VIII, column II). It contained relatively more nickel and less cobalt than the copper-rich liquid. Iron oxide up to about 10 percent and a little silicate was also present dissolved in these sulphide liquids. The composition of the latest sulphide liquid is known from direct chemical analysis of the separated material; it is essentially pyrrhotite with a little copper and cobalt and very little nickel. Over the greater part of the fractionation of the Skaergaard basic magma the sulphide separating was essentially a copper matte; only at a later stage did the sulphide liquid become essentially an iron matte. Nickeliferous sulphides did not develop.

THE BEHAVIOR OF SULPHUR AND CERTAIN CHALCOPHILE ELEMENTS DURING FRACTIONATION

Sulphur.—The Skaergaard intrusion complex can be treated as a closed system for most elements, but for volatile constituents such as water, sulphur, and hydrogen or oxygen, this is not so certain. Being a plutonic intrusion under considerable cover we think, however, that it is unlikely that any significant amount of sulphur escaped during the major part of the fractionation, and this is the assumption on which much of the following discussion is based.

The amount of sulphur in the chilled marginal gabbro is 50 ppm and this is considered to be the amount in the whole original magma. The volume of the intrusion being about 300 km^3 and average density 3 (39, p. 217–24), the total weight of sulphur in the original magma may be estimated as 4.5×10^{7} metric tons. As a result of the fractionation processes the sulphur is now far

TABLE IX

ESTIMATION OF AMOUNTS OF SULPHUR, COPPER, COBALT AND NICKEL IN SUCCESSIVE SILICATE LIQUIDS AND IN THE HIDDEN LAYERED SERIES

Stage	5th liquid	4th liquid	3rd liquid	2nd liquid	1st liquid (=Analysis of chilled gabbro)	Hidden layered series
Part solidified as a percentage	98½	95	88	60	0	
Weight of rock in metric tons	1.4×10^{10}	3.2×10^{10}	6.3×10^{10}	2.5×10^{11}	9×10^{11}	5.4×10^{11}
Weight of sulphur in rock in metric tons	3.6×10^{5}	12.4×10^{5}	8.9×10^{6}	11.7×10^{6}		8×10^{6}
Weight of sulphur in successive liquids, in metric tons	3.6×10^{5}	16 $\times10^{5}$	24.9×10^{6}	36.6×10^{6}		
Ppm S in the liquids	260	350	230	100	50	15
Ppm Cu in the liquids	136	480	519	238	110	27
Ppm Co in the liquids	7	17	41	75	55	42
Ppm Ni, in 5th liquid	13	7	10	125	180	217

Notes. In the original estimate (38, p. 217) the border rocks were taken into consideration, but for present purposes they may be neglected.
Vol. of intrusion = 300 km^3. Assuming a density of 3 the weight of the whole intrusion is $300 \times 10^{9} \times 3 = 9 \times 10^{11}$ metric tons.

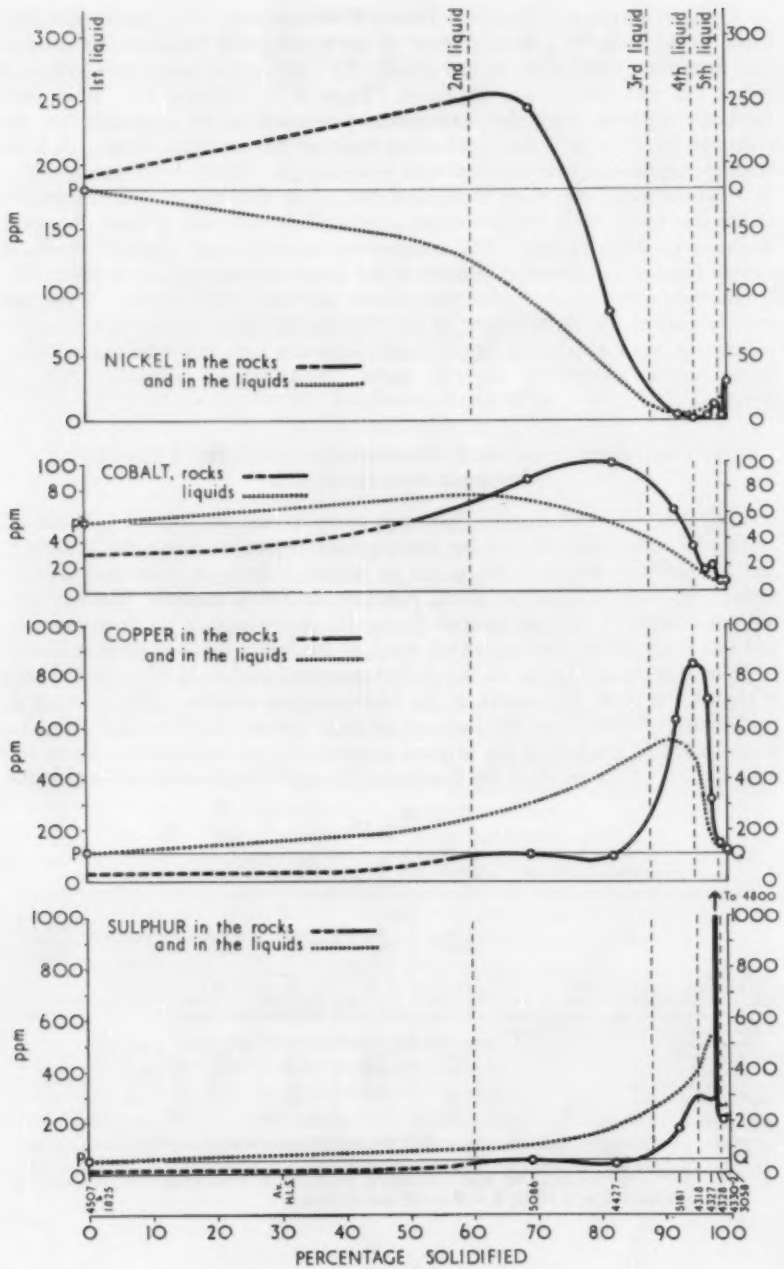

1st liquid
2nd liquid
3rd liquid
4th liquid
5th liquid
ppm
NICKEL in the rocks
and in the liquids
COBALT, rocks
liquids
COPPER in the rocks
and in the liquids
SULPHUR in the rocks
and in the liquids
To 4800
PERCENTAGE SOLIDIFIED

FIG. 16

from equally distributed through the different rocks of the complex (cf. Fig. 15), most occurring in the later rocks, particularly the pyrrhotite band. If the sulphur content of the rocks is plotted, as in Figure 16, against the percentage solidified, the amount of sulphur in the rocks is proportional to the area between S = 50 ppm and the abscissa, and this area represents the total sulphur in the original magma, namely 4.5×10^7 metric tons. For the Skaergaard intrusion the solidification sequence has been arbitrarily divided into five stages (38, p. 214–7). The latest stage, from 98½–100 percent of the magma solidified, produced rocks having a sulphur content proportional to the area between the curve from 98½–100 percent and the abscissa. By multiplying by a suitable factor the area is converted into amount of sulphur in metric tons (Table IX). This amount of sulphur is distributed through 1½ percent of 300 km³ of rock with a density of 3, and from this is obtained the sulphur content, 260 ppm, of the fifth liquid. In the same way the estimated composition of the 4th, 3rd and 2nd liquids, namely 350, 230, 100 ppm, have been obtained. (Table IX). The amount of sulphur in the first liquid, the original magma, is that found by analysis in the chilled marginal rock, namely 50 ppm. The sulphur in the five liquids and the final residual liquid, the acid granophyre, is also plotted in Figure 16, which therefore shows the approximate variation of sulphur in the successive residual liquids from the beginning to the end of the fractionation process in relation to the sulphur content of the rocks.

The right hand part of the graph in Figure 16 is fairly certain, but the left hand refers to the earlier and deeper rocks (the hidden layered series). The amount of sulphur in the total of hidden layered rocks is the difference between the total sulphur in the intrusion and that in the 2nd liquid. This amount is spread through 60 percent of the total intrusion and by this means, the average sulphur content of the hidden layered rocks may be calculated as 15 ppm (Table IX). The graph, Figure 16, for sulphur in the rocks over the range 0–60 percent solidified is therefore drawn with an average content of 15 ppm. It looks as if this is too low, perhaps by a factor of 2, either because our estimate of the volume of the rocks is wrong or possibly because the sulphur in the original magma is underestimated, but it does not affect the general form of the conclusions. The hidden layered series is believed to be comparable with some of the marginal border rocks away from the contact and reference to Table V shows that in rocks from 20 to 200 m from the contact the sulphur content is low.

The estimated amounts of sulphur in successive liquids and in the hidden layered series depend on the relative amounts of the various rock types and their different sulphur contents. In the calculations the amount of the rocks of the pyrrhotite horizon with its high sulphur content is critical. From field observation the thickness of this horizon on Basistoppen is believed to be of the order of 50 m although only about 15 m could be definitely proved. The horizon is now preserved only in a small area and it is not known whether it originally spread over the whole intrusion. Thus the amount of rock belonging to the pyrrhotite horizon cannot be decided on field evidence, and in the

FIG. 16. Sulphur, copper, cobalt and nickel variations in the rocks and contemporaneous liquids during the crystal fractionation.

calculations we have taken a possible figure that gives the hidden layered series a reasonable amount of sulphur. In the light of recent work on the intrusion it is becoming clear that the original estimate of the amounts of the different late stage rocks (38, p. 217) should be revised. Rather than attempt this here we have used the same volumes as were assumed in the original paper except that we have taken the amount of the iron sulphide horizon as being a layer of the observed thickness, 15 m, spread over only the central third of the intrusion. The broader qualitative relationships will not be altered by reasonable alternative assumptions.

A copper-rich sulphide liquid was certainly separating as immiscible droplets in the lower ferrogabbros when about 90 percent of the magma had solidified. At this stage it is estimated that the sulphur content of the liquid was 300 ppm. It is thought that copper-rich sulphide droplets actually formed considerably earlier, when only 70 percent of the magma had solidified and the estimated sulphur content of the magma was only 100 ppm.

Before the separation of immiscible copper sulphide the rocks would not be entirely devoid of sulphur as they would contain the sulphide present in the 30 percent or so of interprecipitate liquid which enveloped the primary precipitate crystals accumulated at the bottom of the magma. Thus before immiscible sulphide liquids formed, the amount in the rock should be roughly a third of the amount in the magma and this is roughly the condition shown in the graph from 0–50 percent solidified (Fig. 16). The amount of sulphur precipitated in the rocks of the hidden layered series was less than the amount present in the liquid and sulphur steadily accumulated in the magma, at least until the point at which copper sulphide liquid separated. During the next stage when immiscible copper-rich sulphide liquid formed, the amount of sulphur separating as immiscible copper sulphide liquid would be considerably greater than before. It would necessarily be such that the silicate liquid remained saturated with copper sulphide. The data and the calculations of the composition of it indicate that the amounts of copper and sulphur in the magma increased as the magma changed its composition due to fractionation. The changes of composition of chief significance in this connection would probably be increasing richness in iron and water. Apparently the solubility of copper sulphide in the changing magma increased until a maximum was reached at 95 percent solidified when the magma at saturation contained about 500 ppm Cu and 300 ppm S.

After this stage the amount of copper in the magma fell, but the sulphur continued to rise. There was not enough copper available to allow the total sulphur separating to exceed the amount in the liquid, so that the amount in the magma continued to rise, until at about 600 ppm sulphur, the solubility of iron sulphide was exceeded and a dominantly iron sulphide liquid separated. The magma after this became rapidly more acid and there was, no doubt, a marked fall in the solubility of sulphide in it.

In the latest stages of the fractionation the clear cut gravitational fractionation resulting in the layered series was replaced by filter-press or other process, visualised as similar to that which gives rise to granophyre in some thick quartz dolerite sills. Sulphides were not precipitated as heavy droplets at

this stage, but seem to have been moved along with the residual silicate fraction. From some rocks, e.g. 4330 and 4332, which are low in sulphur (250 ppm), and others such as 4488, 4489 in which little sulphide mineral can be seen, the sulphide liquid may have been expelled along with the acid silicate fraction giving the final acid granophyre. The acid granophyres carry on the average a few tenths of a percent of sulphides, but, as stated above, this is not regarded as having been dissolved in the acid magma.

Copper.—An estimate of the amount of copper in the magma at the various stages has been made previously (39, p. 140–91) but with the help of the new radioactivation analysis data this has been revised (Table IX) and is presented graphically in Figure 16 along with the amounts in average rocks. When the copper content of the liquid reached 500 ppm the immiscible copper-rich sulphide liquid was certainly forming, and probably it formed earlier when the amount in the liquid was as low as 200 ppm.

Before the stage of copper-rich sulphide formation, some copper entered the primary precipitate olivine, pyroxene and iron ores, and some was present in the interprecipitate liquid. The amounts in these did not equal the amount in the liquid, and thus copper in the successive residual magmas increased.

TABLE X

PARTITION RATIOS (SULPHIDE LIQUID/SILICATE LIQUID) FOR COPPER, NICKEL AND COBALT

	Bornite-rich horizon	Pyrrhotite horizon	Acid granophyre
Cu	1000	120	1
Ni	<100	50	.04
Co	700	20	30

Copper continued to separate in increasing amounts up to 90 percent solidified when the amount in the magma began to fall because more was being precipitated in the rocks than was present in the liquid.

Combining the estimates of the copper in the silicate liquids (Fig. 16) with the estimated amount in the sulphide liquids (Table VIII), partition ratios: $\frac{\text{Cu in sulphide liquid}}{\text{Cu in silicate liquid}}$ may be obtained (Table X). At the bornite-rich horizon this partition ratio is 1,000; at the pyrrhotite horizon it is 120, while at the acid granophyre stage the ratio is apparently about unity. These results are only rough but they are sufficient to show that although copper at the early stages is strongly concentrated in the sulphide liquid phase, this is not so at later stages, a result which so far is unexplained.

Nickel, Cobalt, Palladium, Indium and Gold.—The amounts of Ni and Co in the rocks and the estimated amounts in the silicate magma are shown in Table V and Figure 16. Using the estimates of the composition of the sulphide magma already given (Table VIII) the partition ratios for Ni and Co between sulphide and silicate magma have been estimated (Table X). Although the figure for the first sulphide liquid is far from securely based, it suggests that nickel is not so strongly chalcophile as copper or cobalt.

At the pyrrhotite horizon, these three elements are more nearly equally chalcophile. In the acid granophyre, when the amount of Ni in the silicate melt is for some reason increased after being very low, the amount of Ni in the sulphide becomes unexpectedly low and the partition ratio between the sulphide and silicate melts is far less than unity. Although the Ni in the earlier iron sulphide liquid is small in amount because of the small quantity in the silicate magma, it has, nevertheless, a fairly strong tendency to enter the iron sulphide. This is expected from the occurrence of nickeliferous pyrrhotite ore bodies formed from basic rocks. The pyrrhotite of the acid differentiate is very low in nickel, like the pyrrhotite of hydrothermal ore deposits.

Cobalt behaves differently, the partition at the bornite horizon between copper-rich sulphide liquid and silicate liquid being 700. The close association of cobalt with copper is found in many ore bodies and it may be that this derives ultimately from the ease of entry of Co into a copper-rich melt or copper sulphides. At the pyrrhotite horizon cobalt is 20 times more abundant in the iron sulphide liquid than the silicate, and the same is roughly true at the acid granophyre stage. Thus cobalt does not show a reversal of behavior as nickel does in the latest differentiates.

As a representative of the platinum metals, palladium has been determined despite its very low amounts (Table V). By analogy with the Bushveld and Stillwater complexes it was thought that palladium might be concentrated in the sulphide-rich layers. The original magma has a palladium content of .018 ppm which is the same as that in the standard diabase W-1 (33). The melanocratic rock 5196, rich in bornite, proves to have less palladium than the original magma, so it would seem that there is no strong concentration of Pd in the early copper sulphide liquid. The amount in the fayalite ferrogabbro of the pyrrhotite horizon is .019 ppm, which is only about the same as the amount in the original magma; it is clear therefore that there can be no great concentration of palladium in the iron sulphide liquid relative to the silicate either. Finally, pyrrhotite separated from the acid granophyre, 5275, proved to have less palladium ($<$ .01 ppm) than the rocks with only 0.5–2 percent of sulphide. Thus palladium does not seem to have especially concentrated in the sulphide phase in the Skaergaard fractionation series at any stage of its evolution. The amount of palladium in the three Skaergaard rocks analysed is close to the lower limit of adequate determination by the radioactivation method used and further search for the manner of distribution of palladium in the rocks and minerals has not been undertaken.

The indium content of certain Skaergaard rocks and minerals has been the subject of a recent paper (40) and the data on the rocks are quoted here (Table V). The absence of any concentration of indium in the fayalite ferrogabbro (4328), containing 2 percent of sulphides compared with 4327 with very little sulphide, shows that there is no marked concentration of indium in the immiscible iron-sulphide liquid.

The radioactivation determination of gold in several rocks and minerals of the Skaergaard intrusion by J. H. Crocket has shown a very even distribution in the various rocks and the different minerals separated from them. In an

unpublished thesis Crocket suggests that the gold enters the different silicate and oxide minerals in roughly the same amounts, because it is in the metallic state. There is, however, an increase in gold in the rock 5196, rich in copper sulphide, which suggests a strong concentration in the immiscible copper sulphide liquid forming at this stage. There is no especial concentration of gold in the iron sulphide rich rock 4328, which suggests no marked concentration of gold in the immiscible iron sulphide liquids. The amount of gold in the pyrrhotite separated from the acid granophyre 5275 is .003 ppm (Table III), and that in the pyrite from the acid granophyre (5245) is .016 ppm Au. These amounts are of the same order as in the rock itself (Table V) and indicate again no particular concentration in the iron sulphides.

GENERALIZATIONS AND COMPARISONS

The general conditions for the separation of an immiscible liquid during the cooling and crystallization of a binary system may usually be represented by a phase diagram as shown in Figure 17. In the same way as Niggli usefully indicated the relationships between the essentially nonvolatile silicates and the volatile constituents of magmas such as water by considering them as approximating to a binary system, so we have shown in a thermal diagram the silicates and oxides together as one type of constituent and the sulphides as the other, making in this way an approximation to a binary system. The solubility of sulphide in silicate magma estimated for the Skaergaard intrusion, ranges from 0.01 to 0.05 percent S, that is, about 0.04 to 0.2 percent of copper or iron sulphides. The solubility of sulphide in silicate is so low that the diagram at the scale shown has had to be distorted on the left hand side. The tempera-

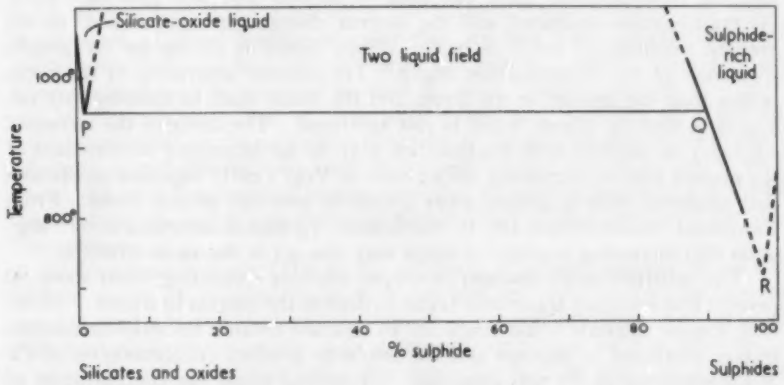


FIG. 17. Generalized diagram for a silicate-oxide and sulphide system treated as if binary. Point P on the evidence from the Skaergaard intrusion lies between .025 and .1 of sulphides, but is shown here as 1% for clarity. Point Q is in the region of 90% sulphide and the other 10% is largely iron oxide. Points P, Q, and R in the natural system would not represent a constant temperature, but extend over a range.

ture when silicates are separating from both silicate and sulphide melts, a temperature given here as constant, must in fact be a range of temperatures in a natural magma. The solubility of oxides and silicates in sulphide is estimated as about 10 percent.[4] From this dominantly sulphide liquid, silicate and oxide separate first, and the sulphides later, under conditions approaching an eutectic.

The nature of the mainly sulphide liquid varies in the Skaergaard case from a mainly copper sulphide liquid to a mainly iron sulphide liquid. Iron is relatively abundant at all stages of the fractionation, and the reason iron sulphide does not form earlier is no doubt that the sulphur concentration is too low. However, fairly early in the differentiation the amounts of sulphur and copper are sufficient to exceed the solubility of copper sulphide in silicate melt. The ultimate appearance of an iron sulphide liquid seems to be due, in a general way to the amount of copper in the magma being small, so that the amount of copper sulphide separating is not sufficient to prevent accumulation of sulphur in the successive residual liquids.

When an immiscible copper sulphide liquid forms in a basic magma the amounts of sulphur and copper in the magma at successive stages of fractionation must be controlled by the solubility of the sulphide liquid in silicate magma. In considering the factors controlling the solubility of the sulphide liquid, we shall assume as a first approximation that the solubility is proportional to the product of the concentration of S and Cu until late in the fractionation when iron sulphide is dominant in the liquid. Immiscible sulphide is believed to have formed in the magma when 60 percent had solidified or even earlier, and from the data summarized in Figure 16, it appears that at this stage, when the liquid was still essentially of ordinary basic magma composition the concentrations were 100 ppm of sulphur and 200 ppm of copper. As fractionation continued and the magma changed in composition, an increased solubility of sulphide in the silicate liquid is shown by the graphs over most of the crystallization stages. The amount separating in the rocks is less than the amount in the liquid and the latter must be continuously adjusted so that the silicate liquid is just saturated. The cause of the increased solubility of sulphide with fractionation may be the increasing iron content of the magma without increasing silica; some of Vogt's early experiments showed that sulphides were in general more soluble in iron-rich silicate melts. From theoretical considerations Dr. P. Bartholomé (personal communication) suggests that increasing amounts of water may also act in the same direction.

The relatively large amounts of copper sulphide separating when about 90 percent had solidified apparently began to deplete the magma in copper. However, copper sulphide liquid continued to separate because the sulphur concentration continued to increase and the solubility product (concentration of Cu $\times$ concentration of S) was exceeded. In general terms the concentration of sulphur in the magma rose, first, because of the increased solubility with the changing compositions of the later residual magmas and then because there was

[4] Since making these estimates of the content of iron oxide and silicate in the sulphide patches we have found that Vogt (34, p. 36–7) estimated that magnetite could be dissolved in considerable amounts in sulphide (about 10%) and that silicate had a very low solubility in sulphide melt (perhaps 1%).

not enough copper relative to sulphur to take out as much sulphur as was then present in the magma. Thus the sulphur content rose until at about 500 ppm of sulphur the solubility of iron sulphide was exceeded. Iron sulphide liquid separating as droplets throughout the magma sank along with certain of the silicate crystals, giving the rock with 2 percent of sulphides. This rock has probably 40 times as much sulphur as could be dissolved in it if melted.

After the formation of the iron-sulphide-rich Purple Band, the changes of composition of the remaining 1½ percent of magma became rapid, and intermediate and acid magmas were produced. Over these stages the solubility of sulphur in the magmas as shown by the curves (Fig. 16) decreases. Vogt's experimental evidence as conveniently summarized by Wilson (43, p. 390–1) indicates decrease in sulphide solubility with increasing silica. The Skaergaard fractionation is such that the silica percentage of the magma is fairly constant up to 95 percent solidified. After this there is a rapid change to higher silica contents and the late fall in sulphur content of the magma is believed to be due to this.

The results of an investigation of the Greenstone Flow of the Keweenawan Series by Cornwall (7, p. 156–9) indicate that during fractionation the sulphur content of the magma was of the order of 200 ppm, with an increase to 250 ppm before a final fall in the latest stages. Copper is similarly about 120 ppm in the magma over much of the fractionation, rising to 170 ppm before a final fall to 70 ppm in the latest acid rock. The solubility of sulphur and copper in the magma are similar to those at the gabbroic stage of the Skaergaard intrusion and the subsequent changes are of the same kind, though less accentuated. Cornwall postulates some loss of sulphur from the system during solidification.

Any basic magma undergoing strong fractional crystallization is likely to reach the stage when the solubility of the sulphide liquid in the silicate liquid is exceeded. Chilled basaltic magmas that are free from accumulations of sulphide droplets and from which loss of sulphide in a volatile form has not taken place, would be expected to have a rather constant amount of copper and sulphur corresponding to their joint solubility. Variation of a limited extent dependent on the overall composition of the magma should also occur. We hope to test this view by analysis for sulphur and copper of basalts that are at different fractionation stages, and also to make experimental tests of the solubility of copper and iron sulphides in fused natural basalts of varying composition.

In Newhouse's study (16) of the sulphides of a large number of normal igneous rocks, the commonest sulphide detected was chalcopyrite, but bornite was not rare. It would seem that sulphur in general separates from igneous rock magmas more commonly as a copper sulphide than as an iron sulphide.

Nickeliferous pyrrhotite and more rarely bornite, in sufficient quantities to be important ores, are associated with certain basic and intermediate rocks in such a way as to suggest their derivation from the igneous magma, and most authors believe that a factor in their genesis is the formation, at some early stage, of an immiscible sulphide liquid phase. Usually the subsequent history of the sulphides is complicated and, indeed, the more economically

important ores have generally been separated from their parent rock, as for instance, the offset ores of Sudbury and the major ore-bodies of Vlakfontein in the Bushveld (26). The less important segregations of sulphides still actually present in the parent igneous rocks provide, however, clearer information on the ultimate genesis of magmatic sulphide ores.

We shall not attempt to review in detail the evidence for and against the ultimate origin of magmatic nickeliferous pyrrhotite ores by the formation of immiscible droplets in silicate magma. Vogt, who contributed so much to the problem himself, summarized the position in 1914 (3, p. 278–300) and again later (35, p. 636–45). He emphasized the significance of certain textural relationships and the tendency of the sulphides to occur near the base of the enclosing igneous rock, a feature he ascribed to the sinking of immiscible sulphide through the magma. He also reviewed relevant evidence available from ore smelting practice and his own experimental work on silicate and sulphide melts. Another valuable review of the problem, mainly from the observational side, is that by Tolman and Rogers (30). Since then Wagner has described "drop-like grains .16 mm across" in the basic igneous rocks of the Vlakfontein nickel area of the Bushveld complex, and ascribed them to liquation prior to crystallization (41, p. 36, 111–3, 129) and with this Schwellnus is in agreement (26, p. 28–9). At a higher level the Merensky Reef also contains 2 percent of sulphides in patches up to 3 mm across which Wagner and Schneiderhöhn also ascribed to immiscibility (42, p. 107, 169, 236–40). The relatively abundant platinum metals occur either in solid solution in the sulphides or as separate minerals. Because the Bushveld is a layered intrusion these occurrences are probably most closely comparable with the Skaergaard case. From Insizwa, Scholtz (24) describes drop-like sulphides near the base of a 3,000 ft thick basic sill and similar drop-like sulphides near the base of basic sills intruded into Carboniferous rock on the east side of the Urals have been recorded (37).

Any immiscible sulphide liquid forming in basic magma apparently crystallized after the bulk of the silicate minerals. Thus there is a tendency for the sulphide patches to be squashed into interstitial relationships with the silicates, or even to vein them, and any original drop-like form may be lost. Also it seems that water and other volatile constituents are present in the sulphide liquid in considerable amounts, and that during the crystallization of the sulphide, these produce hydrothermal alteration of the silicates. Some of the textural features of sulphides in igneous rock, frequently ascribed to replacement of the silicate minerals by sulphide, may be partly the result of the late solidification of the sulphide liquid, combined with subsolidus transformations as described in the appendix and partly the result of hydrothermal alteration of the silicates by water from the sulphide liquid.

If the sulphide liquid does not crystallize until after the bulk of the associated silicates there is the possibility of filter-press action separating both sulphide and silicate liquid from the solid phases, as has been postulated to account for the sulphides in the late acid granophyres of the Skaergaard intrusion. Such a process produces a residual, composite magma of immiscible silicate and sulphide liquids, or a sulphide liquid by itself such as has been

envisaged as responsible for some of the Sudbury (5), Insizwa, Bushveld, and Petsamo nickeliferous pyrrhotite deposits.

The compositions of the sulphides formed in the Skaergaard intrusion are considerably different from the usual magmatic nickeliferous sulphides. One reason for this is that the immiscible sulphides in the Skaergaard magma formed rather late in the fractionation process when nickel had already been largely removed from the magma in the olivine, pyroxene and iron ores of the early layered series (39). Thus by the time the copper sulphides were forming abundantly the amount of nickel in the magma was only 5 ppm and the amount in the sulphide is correspondingly low. In addition it seems that nickel enters copper sulphide liquid less readily than iron sulphide liquid and in the Skaergaard intrusion the formation of an iron sulphide liquid occurred only very late in the fractionation process. Had immiscible iron sulphide formed earlier when the Ni content was that of the initial magma, namely 180 ppm, there is little doubt that the sulphide would have been much richer in Ni and probably comparable with the nickel ores of Sudbury or the Bushveld.

A corollary to this is the hypothesis that the nickeliferous pyrrhotite ore deposits are the product of basic magma initially richer in sulphur than the Skaergaard magma, so that immiscible iron sulphide liquid formed early when the greater part of the nickel was still present in the magma. From the Skaergaard evidence it would appear that the concentration of sulphur in the silicate liquid necessary to produce immiscible iron sulphide liquid is higher than that required to produce copper-rich sulphide liquid. This is confirmed by the thermodynamic reasoning presented in the appendix. In such cases as Insizwa, and Ertili in Norway, where the sulphide is concentrated at or near the base of the intrusion, it seems that the amount of sulphur was such that immiscible iron sulphide liquid was present in the magma at the time of intrusion or immediately afterwards, so that it sank to the base of the intrusion before crystallization of the silicates prevented such movement.

The composition of the Skaergaard magma was such that the first immiscible sulphur liquid was a copper-rich sulphide and it may be that certain bornite-chalcopyrite ore deposits are due to similar conditions. Thus in the Engels Mine, California, there is a deposit of bornite and chalcopyrite associated with a "quartz-norite-diorite" (46% SiO_2) (30, p. 61–4), and in Namaqualand bornite ores, again associated with chalcopyrite, occur as disseminations in mica diorite, hypersthenite and norite (11). In the Keweenawan Greenstone Flow described by Cornwall (7, p. 57) and similar basic sills and lavas of Michigan, bornite and chalcopyrite are ubiquitous but only in small amounts.

Nickeliferous pyrrhotite ores always have some chalcopyrite associated with them. It would seem that early iron sulphide liquid forming in silicate magma can contain considerable amounts of copper as well as nickel. On the other hand the early copper-rich sulphide liquid of the Skaergaard intrusion does not seem to be able to contain much nickel; neither is appreciable nickel reported in the bornite ores of Plumas County or Namaqualand. In the presence of pyrrhotite, chalcopyrite rather than bornite is the stable copper sulphide and magmatic bornite-chalcopyrite ores form a group distinct from pyrrhotite-

chalcopyrite ores. In the Bushveld and Stillwater layered intrusions sulphides are found at different heights within the complexes, the amount of copper in relation to nickel being greater in the higher sulphides. There is also a greater amount of platinum relative to copper associated with the higher sulphides. In the Skaergaard rocks platinum has so far not been determined, but palladium, which is perhaps comparable in amount to the platinum, does not seem to be markedly concentrated in either the copper or iron sulphide liquids of the intrusion. It would clearly be desirable to obtain further data on the relative amounts of minor constituents in sulphides and the igneous magmas from which they have separated.

The question of whether any significant pyrite deposits are due to immiscible iron sulphide separating from basic or intermediate magma (compare, for instance, Roros and Suletjelma in Norway (12, p. 811; p. 3, 304–15)), is more controversial than is the case with the nickeliferous pyrrhotite or the bornite-chalcopyrite ores. In the Skaergaard intrusion both pyrrhotite and pyrite, virtually free from nickel and with relatively low copper, are the final results of immiscibility in the later rocks, and there is the possibility of some iron sulphide ores having been produced initially as an immiscible sulphide liquid in intermediate rocks.

The major constituents of the immiscible sulphide liquid forming from a silicate magma seem to depend on the amount of sulphur in the silicate magma and we have suggested that in magmas with low sulphur a copper matte forms, while from magmas richer in sulphur an iron matte forms. Once the sulphide liquid phase has developed other elements enter with varying ease. From the composition of the nickeliferous pyrrhotite ores it is clear that Ni and Cu readily enter a dominantly pyrrhotite liquid, while the Skaergaard evidence shows that nickel does not readily enter a dominantly copper sulphide liquid. Cobalt behaves differently from nickel and enters abundantly both the dominantly copper and dominantly iron sulphide liquids. The problem of the degree of entry of other elements such as Pt, Pd, etc. into immiscible sulphides is one ripe for investigation (9).

The order of crystallization of phases from the sulphide magma is of interest. From both the copper- and iron-rich sulphide liquids magnetite and small amounts of silicate crystallize first; these were succeeded by the copper or iron sulphides which later inverted or exsolved to give low temperature mineral phases as discussed in the appendix.

The chief factors involved in the separation of immiscible sulphide from magma are (1) the sulphur concentration, (2) the general composition of the silicate magma, especially the amount of iron and silicon in it, (3) the state of oxidation, and (4) the abundance of the chalcophile elements in the silicate liquid. Theoretical approaches to the question of which elements should most readily produce, or enter immiscible sulphide liquids forming in silicate liquids have been made on the basis of relative heats of formation of the oxides and sulphides and other thermodynamic considerations (10 and appendix) and on the basis of ionization potentials by Ahrens (2). What, is much needed, however, is more precise observations of favorable natural occurrences.

ACKNOWLEDGMENTS

The authors wish to thank Mr. D. Mapper and Mr. A. J. Wood of the Analytical Chemistry Group, A.E.R.E., Harwell, for their considerable experimental assistance with the radioactivation determinations of nickel, cobalt and copper. They also wish to thank Mr. S.W.F. Patching of A.E.R.E. for consideration of the problem of whether the sulphides could be extracted by flotation methods and for arranging for Mr. L. D. Mueller and Mr. Pownall to attempt this. Unfortunately with the small amounts of material available, satisfactory results could not be achieved.

Dr. P. Bartholomé, recently a demonstrator in the Department of Geology and Mineralogy, Oxford, has taken a deep interest in thermodynamic problems connected with the Skaergaard sulphides and we are grateful to him for the work embodied in the appendix to this paper.

Professor P. Ramdohr has most kindly examined a number of our polished sections, and has confirmed our identifications of the phases present. One of us (E. A. V.) is particularly grateful to him for the opportunity of learning something of the techniques of ore-microscopy in his laboratory at Heidelberg. For help with certain X-ray determinations the authors thank Mr. P. G. Embrey, British Museum (Natural History) and Mr. K. Heier of Oslo University, at present working in Oxford.

For valuable criticism of the manuscript and particularly for making the suggestion which we later followed up, that certain anomalies in sulphur figures might be due to incipient weathering, the authors thank Dr. H. D. Holland of Princeton, U.S.A., at present National Science Foundation Fellow in the Department of Geology and Mineralogy, Oxford.

Much of the material worked on was collected during the 1953 East Greenland Geological Expedition under the leadership of L. R. Wager and W. A. Deer. For financial assistance towards the cost of the expedition thanks are due to the Royal Society Government Grant Board and the Percy Sladen Fund.

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May 4, 1957

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APPENDIX

THEORETICAL CONSIDERATIONS ON THE SEPARATION OF THE SULPHIDES AND THEIR CRYSTALLIZATION

PAUL BARTHOLOMÉ

COMPOSITIONS OF THE SULPHIDE GLOBULES IN RELATION TO THE CU-FE-S DIAGRAM

The sulphide globules of the Skaergaard gabbros have been shown to have a rather simple mineralogical composition.

In the lower part of the intrusion, they consist of magnetite with three sulphide phases: (a) bornite, digenite and chalcocite (rare); or (b) bornite, digenite and chalcopyrite (common); or (c) bornite, chalcopyrite and cubanite (rare). The globules of composition (b) may also carry small amounts of covellite replacing digenite but this will be neglected for the moment. The chemical composition of the sulphide globules can be plotted—except for the magnetite content—on the Cu-Fe-S diagram as shown in Figure A1. Each globule is represented by a point within one of the triangles corresponding to the ternary associations mentioned above; the point can be located in the respective triangle on the basis of the mineralogical composition. Bornite is generally the most abundant constituent. Chalcopyrite may form up to 50 percent and digenite up to 20 percent by volume. Chalcocite and cubanite are minor. The field of composition of the globules is therefore very long and narrow; it is the area covered by the dotted line AB in Figure A2a.

In the upper part of the intrusion, the globules consist of magnetite, pyrrhotite, marcasite and small amounts of chalcopyrite. The field of composition is the horizontally shaded area on the right part of the diagram (Fig. A2a).

From textural evidence, it is known that most of the magnetite crystallized before the sulphides. It follows that the later crystallization of the globules can be studied in terms of the Cu-Fe-S diagram at liquidus temperatures given by Greig, Jensen and Merwin (3) and reproduced in triangular form and moles percentages in Figure A2c. This diagram shows that only three crystalline sulphide phases can be in equilibrium with a sulphide liquid: (1) a solid solution rich in Cu_2S which may contain up to 25 mol.%Fe; this is called a chalcocite solid solution by Greig et al., but, it is more likely to have

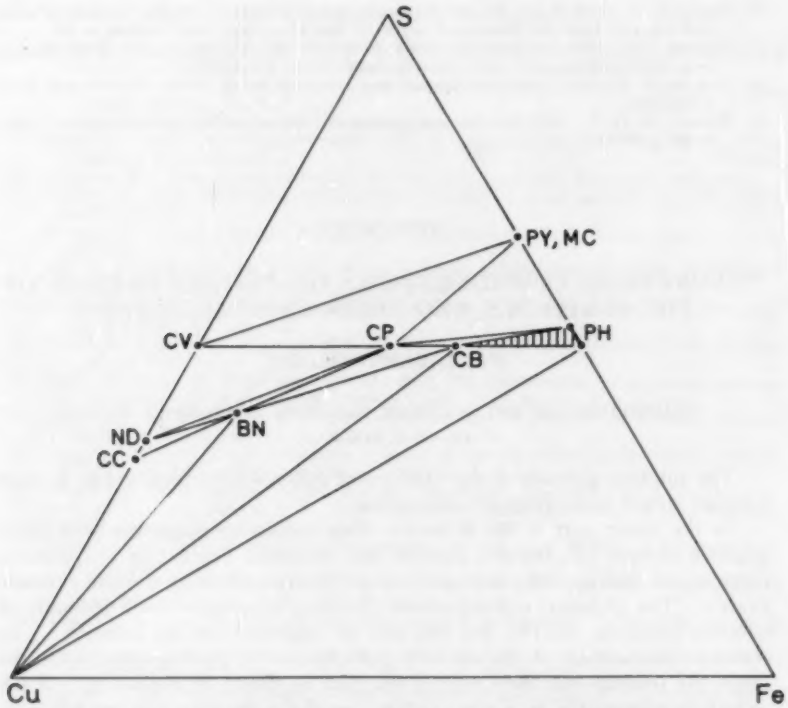

FIG. A1. Tentative Cu-Fe-S diagram at 80° C (Bartholomé, in preparation). Abbreviations:

BN	bornite	MC	marcasite
CB	cubanite	ND	digenite
CC	chalcocite	PY	pyrite
CP	chalcopyrite	PH	pyrrhotite
CV	covellite		

Binary solid solutions are indicated by heavy lines, two-phase fields by vertical shading. The white triangles represent three-phase fields. All compounds are nearly stoichiometric except pyrrhotite and chalcocite. The latter has a range of composition too small to be shown in this diagram.

a structure related to that of bornite or digenite [1] and so will here be called high-temperature bornite; (2) a solid solution richer in iron, the field of which includes the composition of chalcopyrite and cubanite; this has a disordered sphalerite structure (4) and will be called high temperature chalcopyrite; (3) a pyrrhotite solid solution containing a few percent copper.

[1] In addition to the polymorphic transition at 103° C from the orthorhombic to the hexagonal symmetry, chalcocite presumably undergoes another transformation in the neighborhood of 350° C as suggested by an abnormally high heat capacity in that temperature region (5). The high temperature form has the digenite structure (1).

A comparison of Figures A2a and c shows that the globules of the lower part of the intrusion must have crystallized initially into a single sulphide phase, the high-temperature bornite, and in the upper part, they must have crystallized into a pyrrhotite solid solution. Compositions corresponding to high temperature chalcopyrite should be expected in the intermediate zone, i.e. near the base of the Purple Band. They have not been observed. The difficulty of obtaining specimens as well as the erratic distribution of the globules may however account for this apparent anomaly.

SUBSOLIDUS TRANSFORMATIONS

From the preceding paragraph, it follows that the assemblages and textures observed at present in the globules must be the result of subsolidus transformations.

Buerger (2) has shown experimentally that digenite, a stoichiometric compound (Cu_9S_5) below 78° C, has an appreciable range of composition at higher temperatures as shown in Figure A3. Thus on cooling, digenite generally exsolves either covellite or chalcocite. Such an origin is likely for the covellite of the Skaergaard globules that occur exclusively as a secondary product replacing digenite in ternary intergrowths of bornite, chalcopyrite and digenite (main paper, Figs. 6, 8).

The subsolidus transformations in the copper-rich globules have apparently taken place in three successive stages:

(1) breakdown of the high temperature bornite. As no systematic work has been done on the subsolidus of the Cu-Fe-S system, the manner in which this occurred is not known.[2] The final result of the breakdown, however, must be a ternary intergrowth consisting of stoichiometric bornite, chalcopyrite and non-stoichiometric digenite rich in sulphur.

(2) adjustment of the ternary intergrowth to falling temperatures. As cooling goes on, the composition of the digenite gradually changes and approaches the stoichiometric ratio. Meanwhile, the relative amounts of the three phases present vary as shown by the deformation of the triangle ND-BN-CP with decreasing temperature (Fig. A2b): the bornite content decreases, while the chalcopyrite and digenite contents increase. In other words, the sulphur made available by the transformation of digenite reacts with bornite to form more digenite and chalcopyrite.

(3) appearance of covellite. At a given temperature, which may be of the order of 150° C, one of the steps required for the maintenance of the equilibrium according to the above reaction can no longer take place at a sufficient rate. Digenite simply exsolves covellite and eventually reaches the stoichiometric composition.

[2] Some of the textures observed are of interest in this regard. The globules which have a composition close to point B in Figure A2a (about 50% bornite and 50% chalcopyrite) do not consist of a homogeneous intergrowth. They show independent grains of pure chalcopyrite in contact with a bornite containing 15 to 20 percent chalcopyrite lamellae. This suggests, by comparison with the textures found in metals and alloys (11), that the bornite-chalcopyrite binary system is characterized by a eutectoid point and not a solvus. Schwartz (12) has already mentioned this possibility.

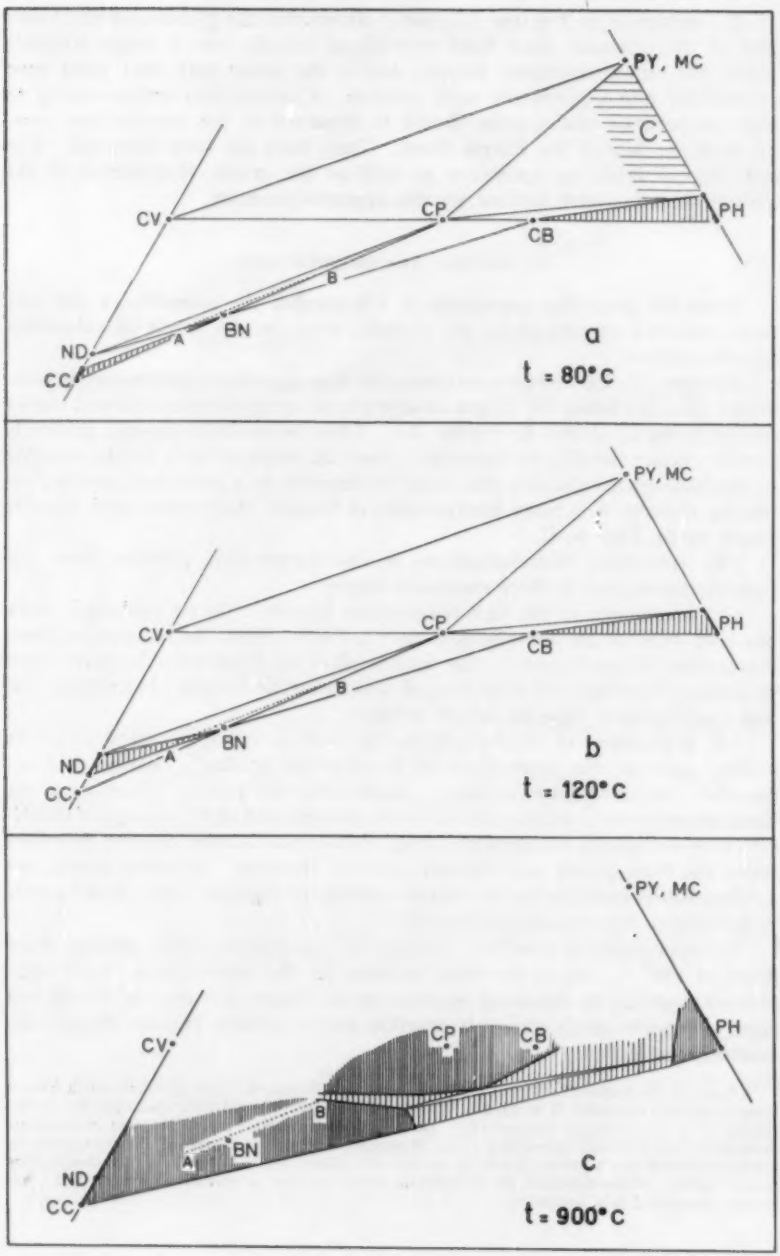
PY, MC
C
CV
CP
CB
PH
B
BN
A
ND
CC
a
t = 80°C
PY, MC
CV
CP
CB
PH
B
BN
A
ND
CC
b
t = 120°C
PY, MC
CV
CP
CB
PH
B
BN
A
ND
CC
c
t = 900°C

FIG. A2.

The initial sulphide mineral to form from the sulphide globules separating in the upper part of the intrusion was probably a copper-bearing pyrrhotite. The present phases are the result of exsolution of chalcopyrite and later alteration to marcasite.

The globules in the lower part of the intrusion consist of four phases (except for the disequilibrium assemblage involving covellite), the maximum number allowed by Goldschmidt's phase rule. This indicates, as shown by Korzhinski (6), that the subsolidus transformations described took place in a closed system. On the other hand, some of the globules in the upper part of the intrusion consist only of marcasite and chalcopyrite. They must have cooled down in a system open either to sulphur or to iron, most probably to iron as shown on the basis of volume considerations by the authors of the main paper.

EQUILIBRIUM BETWEEN THE SILICATE AND SULPHIDE LIQUIDS

It is certain that the primary crystallization of the globules also took place in open systems because, at the temperatures involved (900° C), the reaction rates between sulphide liquid, silicate liquid, and crystalline phases are very large as shown by metallurgical operations. Thus, throughout the magmatic stage, the composition of each individual globule varied in such a way that equilibrium with the environment was maintained. The number of phases after completion of the crystallization is given by Korzhinski's phase rule: $P_{max} = C-F$ where P_{max} is the maximum number of phases, C the number of independent constituents, and F the number of components whose activities or partial pressures are determined by external constraints on the system (6).

In the Skaergaard case, the maximum number of phases is three because there is such a constraint: the partial pressures of oxygen P_{O_2} is controlled by equilibria between the primary precipitate and the liquid or liquids. These equilibria can be written for the lower gabbros which contain olivine, pyroxene and iron oxide:

$$6\ \langle Fe_2SiO_4\rangle + (O_2) = 6\ \langle FeSiO_3\rangle + 2\ \langle Fe_3O_4\rangle$$

FIG. A2. Presumed phase relations in part of the Cu-Fe-S triangle at various temperatures.

Abbreviations as in Fig. 1. Binary solid solutions are indicated by heavy lines, two-phase fields by light vertical shading, one-phase fields (areas of ternary solid solution) by heavy vertical shading. The white triangles represent three-phase fields.

Fig. A2a is simply an enlargement of the middle part of Fig. A1. The ranges of composition of pyrrhotite and chalcocite have been shown, as well as the resulting two-phase fields. Fig. A2b shows how the relations between chalcocite and digenite change with increasing temperature (see Fig. A3). Fig. A2c, after Greig, Jensen and Merwin (3), shows the ranges of composition of the three sulphide solid solution high-temperature bornite high-temperature chalcopyrite and pyrrhotite solid solution at temperatures just below the solidus (900° C).

The dotted line AB represents the composition of the globules in the lower part of the intrusion. The horizontally shaded area C in Fig. A2a represents the field of composition of the globules in the upper part.

and for the quartz-bearing fayalite ferrogabbros:

$$3\ \langle Fe_2SiO_4\rangle + (O_2) = 2\ \langle Fe_3O_4\rangle + 3\ \langle SiO_2\rangle$$

where parentheses ( ) refer to a compound dissolved in the liquid, and angular brackets ⟨ ⟩ to a compound present in a crystalline phase, either a ferromagnesian silicate or an iron-titanium oxide or a form of silica. Preliminary calculations made by the writer show that, during the crystallization of the Skaergaard intrusion, P_{O_2} remained in the range of 10^{-12} to 10^{-10} atmosphere.

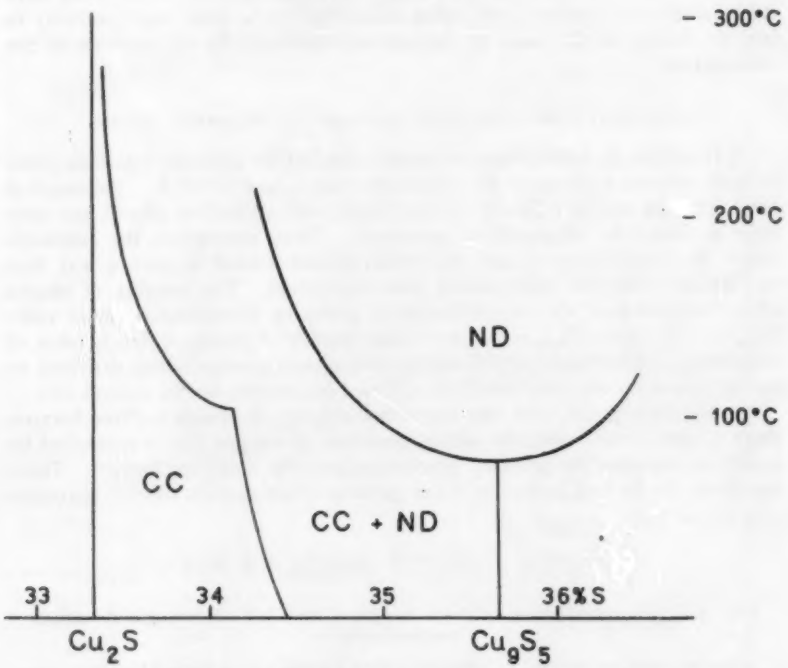

FIG. A3. Part of the Cu-S binary system after Buerger (2).

In addition to P_{O_2}, three other parameters define the thermodynamic state of the globule at a given temperature: the partial pressure of sulphur P_{S_2}, and the activities of iron and copper. Sulphide liquids are generally thought to have structures rather similar to those of sulphide crystals. Thus, as a first approximation, the specific free energies of the crystalline sulphides may be used in thermodynamic calculations involving melts, as is usually done by metallurgists, and it becomes more convenient to choose a_{Cu_2S} and a_{FeS}, the activities of the cuprous and ferrous sulphides respectively, in addition to P_{O_2} and P_{S_2}, to define the state of the globule. The pure, solid compound (Cu_2S

or FeS) in equilibrium with the metal (Cu or Fe) is chosen as the standard state so that the activity of the compound is the same in the two liquids and in all the solid phases present.

Schuhmann and Moles (10) have measured the sulphur pressures in equilibrium with liquid copper sulphides of various compositions at temperatures of 1150 to 1350° C. Their diagram shows that, at a given temperature, P_{S_2} increases by a factor of about 100 for each mole percent of sulphur added to the liquid. One might therefore expect that, in iron-copper mattes also, P_{S_2} would be extremely sensitive to variations in the sulphur content. Line AB in Figure A2 would be a line of equal or slowly varying partial pressure of sulphur, since the sulphur content of the magma [3] does not change appreciably during the crystallization of the lower and middle gabbros (see main paper). During the Purple Band stage, on the other hand, P_{S_2} might be expected to rise sharply.

The activity of FeS is related to other thermodynamic parameters because of the following equilibrium:

$$3\ (FeS) + 2\ (O_2) = \langle Fe_3O_4 \rangle + \frac{3}{2}\ (S_2) \qquad (1)$$

Using the thermochemical data used by Kubaschenski and Evans (8) and Kubaschewski and Caterall (7), the standard free energy change of this reaction is found to be (in calories):

$$\Delta G^\circ_1 = -\ RT \ln K_1 = -\ 155{,}000 + 38.50T$$

where

$$K_1 = \frac{P^{\frac{3}{2}}_{S_2}}{a^3_{FeS}\ P^2_{O_2}}$$

At magmatic temperatures, say 900° C, K_1 is of the order of 10^{20}. It follows that if P_{O_2} remains close to the value of 10^{-11} given earlier,

$$a_{FeS} = 5\sqrt{P_{S_2}} \qquad (1a)$$

The uncertainty may be of a factor of 10.

FeS and Cu_2S are completely miscible in the liquid state and form extensive solid solution at high temperatures. This suggests that their solution (liquid) is nearly ideal, which is confirmed by experiments recently carried out by Professor Terkel Rosenqvist.[4] So, as a first approximation, a_{FeS} is

[3] The decreases of temperature and total pressure should also be taken into consideration if better thermochemical data allowed a more rigorous analysis of the equilibrium.

[4] I am indebted to Prof. Terkel Rosenqvist for the following information which is still unpublished:

In mattes saturated with magnetite, the oxygen solubility increases with increasing iron content and is appreciable for pure iron sulphide. In the copper-rich and oxygen-free mattes, the activity of copper sulphide follows Raoult's law provided that the molar concentrations are computed in terms of FeS and $CuS_{0.5}$. Computing them in terms of FeS and Cu_2S would conceal the ideality of the solution.

equal to the concentration of FeS in the sulphide melt:

$$a_{FeS} = \frac{(FeS)}{(FeS) + (CuS_{0.5})}$$

which can be evaluated on the basis of the composition of the globules. During the first part of the crystallization, a_{FeS} varied between 0.1 and 0.2, and P_{S_2} roughly between 0.0004 and 0.002 atm. At the Purple Band stage, a_{FeS} became close to unity and P_{S_2} reached a value of 0.04 atm. These figures reflect the pressure increase due to the increase in sulphur content of the magma during the same period.[5]

Another equilibrium of interest is that controlling the distribution of copper and iron between silicate and sulphide liquids, called slag and matte respectively by metallurgists. It is one of the most important equilibria of copper metallurgy and will be written here following Schuhmann (9):

$$(Cu_2O) + (FeS) = (Cu_2S) + (FeO) \qquad (2)$$

The magma or slag is not a pure oxide and the matte not a pure sulphide liquid. However, the metal atoms are mostly surrounded by oxygens in the slag and by sulphurs in the matte; moreover the free energies of formation of iron and copper silicates from the oxides are not large, so that, as a first approximation, equation (2) may represent the matte-slag equilibrium.

The standard free energy change for reaction (2) at temperatures of 700 to 1000° C is:

$$\Delta G^\circ_2 = -RT \ln K_2 = -24{,}000 + 5{,}000 \text{ cal.}$$

whence, at 1000° C,

$$K_2 = \frac{a_{Cu_2S} \times a_{FeO}}{a_{FeS} \times a_{Cu_2O}} \simeq 10{,}000 \qquad (3)$$

The standard states are taken as the pure solid for Cu_2O, and as wüstite in equilibrium with iron metal for FeO. Equation (3) may also be written:

$$\frac{a_{Cu_2O}}{a_{FeO}} \simeq \frac{1}{10{,}000} \frac{a_{Cu_2S}}{a_{FeS}} \qquad (4)$$

As shown by Turkdogan and Pearson (13), the activity of FeO in a complex silicate melt is approximately equal to its molar concentration as long as sufficient amounts of divalent cations such as Mg, Mn, and Ca are present. On the other hand, the activity of Cu_2O, which is quite a minor constituent of the silicate melt, may be expected to be proportional to its molar concentration according to Henry's law. During the crystallization of the lower and middle gabbros, the right hand side of equation (4) remained almost constant, as

[5] The uncertainty of the coefficient of equation (1a) is mostly due to inaccuracies in the values of the free energies of formation of magnetite and pyrrhotite. Therefore, although the absolute values of P_{S_2} might be inaccurate by a factor of 100, the increase mentioned here is significant.

shown by the composition of the globules, so that the Cu_2O and FeO contents of the silicate melt must have varied proportionately.[6]

The data given in the main paper indicate such a relationship. During the Purple Band stage, on the other hand, the right hand side rapidly decreases while a_{FeO} keeps increasingly slowly. The sharp decrease in the copper content of the magma mentioned in the main paper can account for these variations.

CONCLUSIONS

(1) The mineralogy and textures observed in the sulphide globules of the Skaergaard gabbros are the result of subsolidus transformations.

(2) Thermodynamic calculations made on the basis of the composition of the globules give an independent confirmation of the results obtained in the main paper concerning the sulphur and copper contents of the magma during the differentiation.

ACKNOWLEDGMENTS

I wish to thank Professor L. R. Wager for introducing me to the problems of the Skaergaard sulphides which awakened my interest in sulphide geology, and to him and to Dr. H. D. Holland for many helpful discussions. I also thank them, as well as Dr. E. A. Vincent, for critically reading the manuscript.

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May 4, 1957

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[6] The decreases of temperature and total pressure should also be taken into consideration if better thermochemical data showed a more rigorous analysis of the equilibrium.

Economic Geology
Vol. 52, 1957, pp. 904–913

URANIUM DEPOSITS IN WESTERN NORTH DAKOTA AND EASTERN MONTANA

DONALD TOWSE

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ABSTRACT

Exploration in the lignite basin in western North Dakota and eastern Montana followed discovery of trace amounts of uranium in Paleocene lignites. Proved and probable reserves of more than 200,000 tons of lignite containing more than 0.10 percent uranium oxide have been developed.

Bedded and lenticular deposits in both lignite and sandstone beds were concentrated by circulating ground water.

Most of the uranium is in complex carbon-uranium compounds. Metatyuyamunite and autunite are common secondary minerals. Ore deposition is controlled by carrier bed permeability, by host-rock petrography, and by structure.

The milling of lignite to produce a metal is a difficult process to perfect. Progress in milling is necessary before this potential uranium reserve can become an economic ore.

INTRODUCTION

EXPLORATION and development have been quietly going on for three years in a uranium mineral belt in Western North Dakota. In spite of legal obstacles, normal problems associated with a new area, and formidable metallurgical difficulties, operators there have proved uranium in lignite beds in excess of 200,000 tons of ore-grade material. This estimate is based on ore reserves known to the writer and on extrapolations based on the activity of others. The estimate is believed to be conservative. More exploration and more re-

serves should be proved in the future when mining and milling processes are developed.

This report is based on exploration and development done by and under the writer's direction between June, 1954 and August, 1956.

HISTORY OF DEVELOPMENT

Trace amounts of uranium were first reported in the lignite basin of the western Dakotas and eastern Montana by members of the U. S. Geological Survey working on trace elements investigations for the Atomic Energy Commission. That work was done between 1951 and 1953, and only traces of uranium were found in the lignites. Denson and Gill and their colleagues have recently summarized that trace elements work (1, 2).

The writer began the first systematic program of commercial uranium exploration in the region in North Dakota in June, 1954. That work was interrupted in August and September during the rush to exploit discoveries of high grade uranium-bearing lignites in Harding County, South Dakota, just south of the areas described in this report. Development in the North Cave Hills in Harding County was rushed, and King (3) has reported on mineable deposits there and reserves exceeding 100,000 tons.

The first discovery of a commercial grade ore body in North Dakota was made during our mobile radiation surveys in September, 1954, on the Lawrence Smith ranch in eastern Billings County. Six hundred tons of uraniferous lignite has been produced from that deposit and sold under contract to the Atomic Energy Commission.

Preliminary Exploration. The trace elements investigations had proved, before 1954, presence of weakly uraniferous lignite in the highest beds underlying buttes of Oligocene White River formation in South Dakota and southwestern North Dakota. Points 1, 2, and 4 on Figure 1 are three buttes in which radioactive lignites were mapped during those investigations. In addition, the volcanic ash beds in the overlying White River formation had traces of uranium.

Those discouragingly small amounts of uranium were considered significant and sufficient to indicate that ore might be found in the region. In addition, the many lignite beds, intertonguing terrestrial beds, dirty and carbonaceous sandstone, and the wide occurrence of volcanic ash and debris in the Paleocene and Eocene rocks in the district, indicated favorable ground.

Ground Water Analyses. One theory of uranium accumulation is that it is concentrated by ground water from traces in volcanic materials. In addition, uranium is known to be soluble in bicarbonate waters. In order to narrow the search in such a broad area, ground-water analyses from state and federal records were compiled, plotted, and contour maps constructed. Leaching of the acid volcanic rocks in the region would give the leach waters a high sodium content as compared to calcium and magnesium. Accordingly, one map was constructed showing the ratio of total sodium to calcium and magnesium in the groundwater. Fortunately, many data were available and most of the aquifers were in the Paleocene Fort Union rocks.

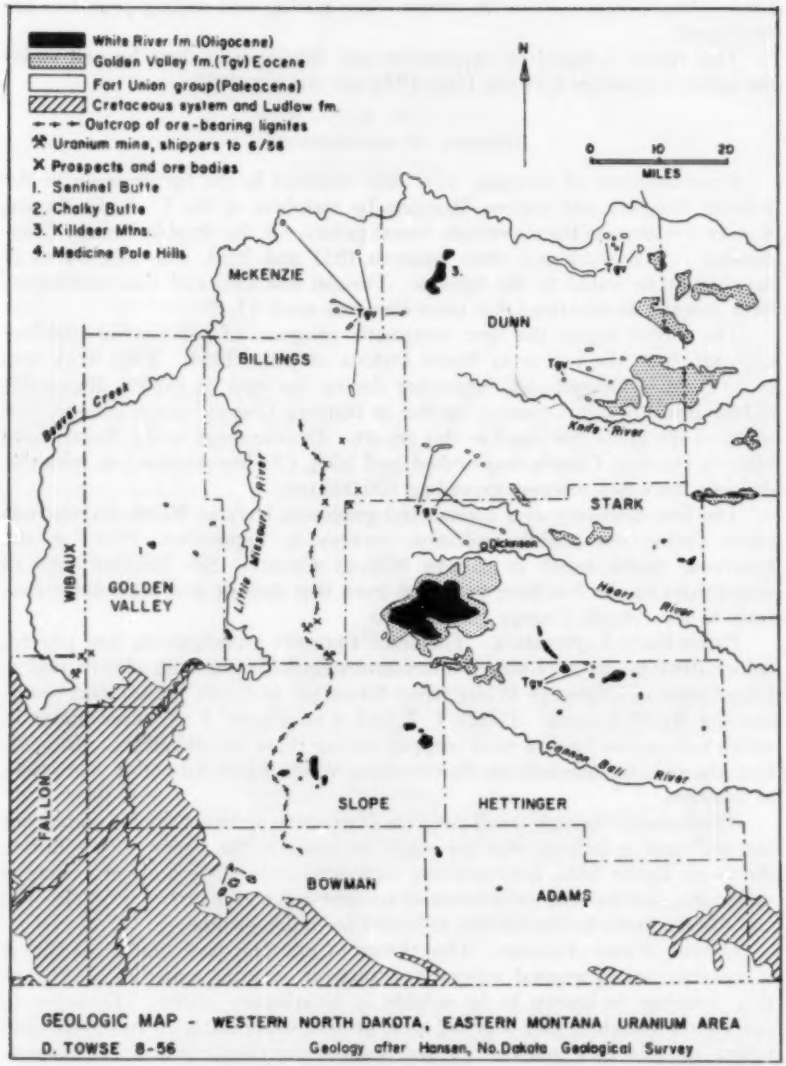


FIG. 1.

The highest values on the sodium-ratio map outlined an area in western Stark and eastern Billings County, North Dakota. The highs were along a north-south trend of about 40 miles, centered near the town of Belfield. That area also had the highest bicarbonate content and a high fluorine content. Our

first exploration was concentrated in that region, and most of the subsequent discovery and development has been there.

GENERAL GEOLOGY

Most of the region is covered by the drab terrestrial sandstones, shales, and lignites of the Paleocene Fort Union formation. Structurally, this is the west rim of the Williston Basin, with the Cedar Creek anticline to the west in Fallon and Wibaux Counties, Montana. The regional surface dip is northeast, and folding is gentle. Structures are gentle folds, broad basins, and anticlinal noses. Dips are measured in a few tens of feet per mile.

The valleys of the Little Missouri River and its tributaries are deeply eroded badlands, but most of the rest of the land is gently rolling upland crop and pasture land with a thin soil cover. The uraniferous beds are best exposed and were first found along the good outcrops on the east edge of the badlands.

Isolated buttes and ranges of hills formed by the overlying Eocene sands and clays of the Golden Valley formation and the Oligocene White River clays, limestones, and ash beds rise above the general level of the upland.

There is an erosional disconformity on the top of the Fort Union, and the early government work indicated that uranium would be found in the highest lignites lying below that disconformity. The highest lignites are preserved only under the Eocene and Oligocene hills and buttes. A great deal of rim flying and ground exploration has proved that the lignites in the buttes are below ore grade and that the higher uranium concentrations are in thicker lignite beds a little lower in the stratigraphic section. The high grade uraniferous beds crop out in the rim of the badlands and in a few low places on the upland.

The ore-grade material is found in lignite beds in the upper part of the Sentinel Butte member of the Fort Union formation. These beds have not been traced continuously from the uranium areas in South Dakota, but they probably lie 200 to 300 feet stratigraphically higher than the ore-bearing "E" lignite bed in the Cave Hills. The uraniferous beds generally crop out at or above 2,800 feet above sea level in Billings County.

Deeper drilling and prospecting in the lower part of the section has not, as far as we know located any ore in lower parts of the formation.

The uranium occurs in thin lignite seams that are no more than 6 feet thick. The ore-grade material in the lignite rarely attains a thickness of over two feet. Most of the uranium in the lignites is combined in an un-named uranium-carbon complex "mineral" intimately tied up in the lignite structures. The lignites themselves have a high ash and moisture content. Most burn poorly or with difficulty. The uranium-bearing lignites are of two types, a soft almost structureless kind, and a dense woody black lignite. One uranium occurrence is in a lustrous spintery lignite like some of that in the deposit in the North Cave Hills.

Secondary autunite forms on joint and bedding planes in some deposits. Other accessory minerals are pyrite, jarosite, gypsum, and calcite. Ore assays

range from 0.10 to selected samples containing 18 percent uranium oxide. Some sands and clays are mineralized in thin contact zones next to high-grade uraniferous lignites. Ore-grade deposits will average from 0.15 to 0.30 percent uranium oxide.

The uraniferous beds occur in two general lignite horizons. These are probably not continuous beds, as drilling and outcrops show a typical interfingering and lensing in the lignite beds. The two lignites are separated by about 50 to 60 feet, and they are overlain and separated by generally sandy units containing thin clay beds.

The upper lignite varies from a few inches to 3 feet in thickness. The lower bed is generally from 2 to 6 feet thick. Both lignite zones are underlain by dense bentonitic underclays. The upper bed contains a perched water table on the upland; it supports small springs along its outcrop on the edge of the Little Missouri valley.

In general, the ore bodies in the upper zone are thinner, smaller, and more lenticular than those in the lower zone. The uranium deposits and prospects are concentrated in two general areas. One is in southeastern Billings County; the other is in the east central part of the county north of U. S. Highway 10.

BLANKET LIGNITE URANIUM DEPOSITS

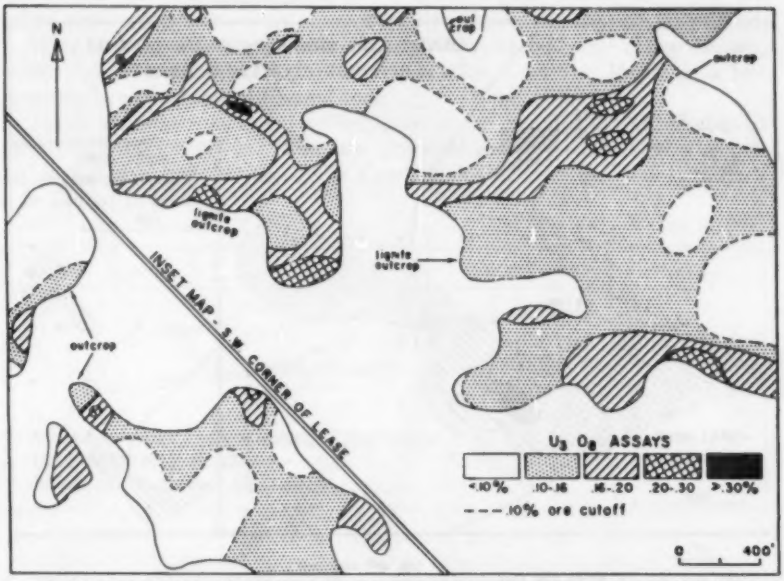
Two general types of uranium deposits can be recognized. One is a blanket type body, characterized by relatively uniform mineralization over a large area. Thickness changes are mostly small. Other deposits are smaller, vary in thickness and grade, and are in irregular shapes. They are generally of higher grade than the blanket deposits; they are called lenticular deposits in this report.

Figure 2 shows uranium concentration on one large blanket deposit in Billings County. On this property, of 100 acres of lignite, 86 acres contain lignite containing more than 0.10 percent uranium oxide. Total reserves are in excess of 150,000 tons; average assay is 0.15 percent U_3O_8; average ore-grade thickness is 1.78 feet; and overburden varies from 5 to 22 feet and will average 13 feet.

The lignite bed is 2 to 6 feet thick, but only the upper 1 to 2 feet are of ore grade. The upper mineralized part of the lignite is more porous and less dense than that below. The upper surface is slightly irregular and intergrades with overlying brown carbonaceous shale. The lignite is underlain by a thick bentonitic clay, and the uraniferous lignite is oxidized, as evidenced by much interbedded jarosite. The lignite is easily stripped by dozer and mined with a front-end loader.

Radioactive equilibria are such that a chemical assay is 1.40 times the radiometric. This ratio increases in the low-grade uraniferous lignite below the ore zone. In addition, the assay ratio also increases in one place in the direction of present water flow, under a surface swale that leads toward springs on the outcrop in a gully. The ratio increases close to the springs and the outcrop. The ore is about 5 feet above the present water table.

The mineralized thickness varies very little, and the small variations are irregular. The round barren patches, where exposed, have been places where the lignite changes from a bedded and structured type to a soft, powdery, structureless black soil. Those changes are probably due to original differences in the deposited lignite.



BLANKET TYPE URANIUM-LIGNITE DEPOSIT BILLINGS COUNTY, NO. DAKOTA

FIG. 2.

LENTICULAR LIGNITE URANIUM DEPOSITS

The lenticular deposits are more co .mon than the blanket ones, and they are typical of the deposits in the upper of the two uranium lignite levels.

Figure 3 is a map and cross section of a lenticular uranium deposit in the upper lignite level in Billings County. This deposit contains about 1,500 tons of lignite containing 0.25 percent uranium oxide. The lignite is overlain by a sandstone bed and thin clay bed, and is underlain by a dense clay. (Note the 25-fold vertical exaggeration of scale in the cross-section.) The lignite grades into and interfingers vertically and laterally into a brown carbonaceous clay. In some places no lignite is found, and only brown clay is present. Those changes are typical of the upper lignite level in this area.

As the Figure shows, other small deposits are indicated by drilling on the same property. These lenticular deposits have commonly been found in groups or clusters such as this.

The lenticular deposits may change rapidly in thickness. They may be of any size; some hold only a few hundred pounds of ore. Some of the smallest deposits are very high grade. In the deposit illustrated, grade varies with lignite thickness; the same is true in other deposits.

In some uranium bodies, there is a striking correlation between uranium content and permeability of the overlying beds. Where the overlying beds

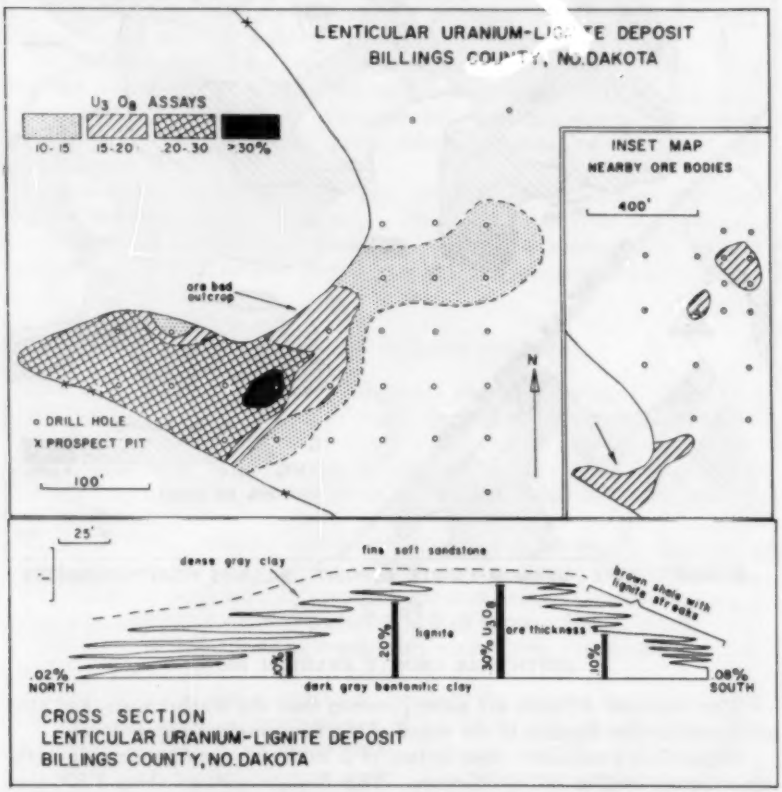


FIG. 3.

are permeable sandstone, the uranium content is higher; it is low where shale covers the lignite. In one deposit, uranium oxide content in lignite under sandstone varies from 0.09 to 0.31 percent U_3O_8; assays in the same lignite bed under shale ran from 0.06 to 0.11 percent. The assay content is roughly in inverse relation to shale thickness.

In one deposit, where the mineralization is at the level of the ground water table, the uranium, iron, and lime content varied together. High grade mate-

rial has as much as 10 percent lime. This unusually high lime content for lignite was probably introduced into the lignite with the uranium.

SANDSTONE URANIUM DEPOSITS

The highest sandstone bed in the Fort Union formation is abnormally high in both uranium and lime in parts of the lignite region, but no sandstone ore bodies are known in the same area where lignite uranium deposits are found.

West of the general lignite uranium area, in western Goden Valley County, North Dakota and in nearby Fallon and Wibaux Counties, Montana, a few prospects have been found in sandstone.

These sandstone prospects probably lie in the Sentinel Butte member of the Fort Union formation. They are clustered near some small anticlines on the shallow east flank of the Cedar Creek anticline. All the prospects seem to be similar in geology.

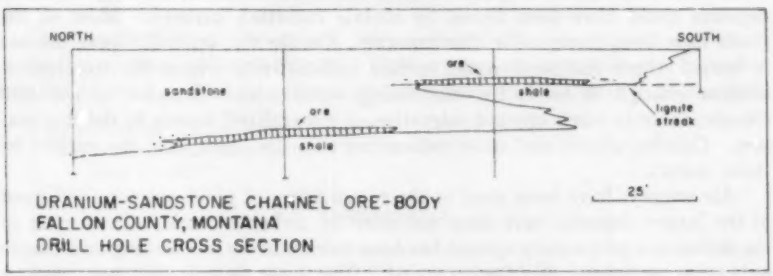


FIG. 4.

One ore body was drilled and excavated and studied in detail. A cross section is shown in Figure 4. The ore occurs in a thick sandstone bed, but it is concentrated near the base of the bed, in channel-shaped deposits where the sandstone grades to shale and lignitic shale. The rock is dirty, carbonaceous, and rusty where mineralized. It has a slight yellow bloom from the ore mineral meta-tyuyamunite. A trial shipment of ore was sent to Edgemont, South Dakota. The pit is now shut down.

This type of ore body is the kind originally anticipated in the district, and it shows the possibility of developing ore in rocks other than lignite in the region.

SUMMARY

The uranium was probably introduced into the lignite by normal ground waters after solidification of the lignite. Relation of grade changes to present water tables suggests that enrichment and migration of uranium is happening at present. One theory is that the uranium came from vertical leaching from overlying beds (4). The occurrence of lower ore-bodies under impermeable rocks seems to rule out this theory in some deposits.

The correlation between mineralization and permeability of surrounding rocks supports a normal ground water origin. That correlation makes a useful guide to development.

It was early found that many prospects were on the higher hills in the district. The major ore belt lies along a generally higher ridge on the drainage divide between the Little Missouri and the Heart-Cannonball watersheds. Some of the hills are now known to be topographic expressions of folds, and one group of prospects is proved by surface mapping to lie along the axis of a broad anticlinal nose. As more information and drilling develop, an anticlinal or structural hypothesis may be a useful guide to ore.

Within individual uranium deposits, the grade varies with small scale variations in stratigraphy and petrology of the host rock.

EXPLORATION METHODS

Due to the network of good roads in the district, most of the large uranium deposits could have been found by mobile radiation surveys. Most of the roads have been surveyed in this manner. On the flat upland, where the ore is buried, there has been some surface radioactivity where the uranium is shallow enough to be in the circulating water zone. Because of the arid climate, there is much upward migration of mineralized waters in the dry season. Caliche, alkalis, and some radioactive salts are brought to the surface by those waters.

Air surveys have been used in the rough areas of good outcrop, and most of the larger deposits have been indicated by airborne work. Over most of the flatlands a grid survey system has been used, and both recording and simple indicating equipment has been carried. The same factors that help surface surveys make such air surveys valuable. Many of the airborne anomalies on the upland are of low magnitude, but analysis of the frequency and distribution of those anomalies has been successful in outlining new uranium areas.

Rotary drills have been used almost exclusively in development. With slight modifications of normal Colorado Plateau practice, it has been possible to obtain good holes and samples and cores from even the softest of ores. The ground becomes wet at moderate depths and is loose, so wagon drilling would probably be unsatisfactory. Most drill units have large capacity air compressors for most of their drilling and stand-by equipment for drilling with water in wet ground.

PRODUCTION AND MILLING

Production has been small. Some deposits have been drilled in preparation for mining but the only market for uraniferous lignite has been in pilot processing plant work for the Atomic Energy Commission. The Commission has bought 1,700 tons from local deposits.

Early in the lignite program it was found that raw lignite leached well but was impossible to filter satisfactorily in conventional mill processes. A great deal of government work is being done to perfect a process. One process has been developed on a laboratory scale and is being tested in pilot plants.

Preparatory to leaching, the raw lignite must first be sintered to remove oils and tars and to make it amenable to more conventional leaching and separation (5).

No large scale mining will be started until a competitive process is developed.

CONCLUSION

Development is being aimed toward more high grade lignite to raise the average grade of the mill feed to a profitable level.

No real attempt has been made as yet to extend the ore belt to neighboring provinces where geologic conditions are similar.

The experience and data gathered in the present initial phase of exploration will, when needed, be useful when progress in milling methods makes an economic ore of this large potential uranium resource.

ACKNOWLEDGMENTS

The cooperation of the clients who released the information contained herein is acknowledged with thanks. Drafting and stenographic services were supplied by the Department of Geology, University of California, Los Angeles.

UNIVERSITY OF CALIFORNIA,
LOS ANGELES, CALIFORNIA,
May 7, 1957

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Economic Geology
Vol. 52, 1957, pp. 914–922

LEAD ISOTOPE COMPOSITION OF PERUVIAN GALENAS[1]

J. LAURENCE KULP, G. C. AMSTUTZ, AND F. DONALD ECKELMANN

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ABSTRACT

Isotopic abundance measurements have been made on the lead from nineteen galena samples covering a wide range of geographical and geological settings in the Tertiary hydrothermal mineralization of the Central Peruvian Andes. The results are strikingly similar, suggesting origin from a homogeneous magmatic source derived from an average crustal environment with regard to its U/Pb and Th/Pb ratios. The consistency of the lead isotopes through all zones of mineralization and over great vertical and horizontal extent is further evidence against significant fractionation of these isotopes during transportation and deposition.

INTRODUCTION

A RECENT worldwide survey of the isotopic composition of lead ores by Bate, Gast, Kulp, and Miller (3) has shown that in some areas there may be significant differences in the relative abundances of lead isotopes. An intensive study of the lead isotope composition of the Southeast Missouri Lead Belt by Eckelmann, Kulp and Brown (5) has shown that large variations exist, which can be systematically related to the pattern and relative ages of ore in a single district. The evidence in Southeast Missouri suggests inhomogeneous extraction of lead from moderate crustal depths. This pattern appears to be the same for the entire Mississippi Valley where the lead ores cannot be conclusively associated with major igneous intrusions. Other districts related to igneous intrusives, such as along the eastern border of the Boulder Batholith, do not show significant variations in the lead isotope abundances of galena samples (Wright, personal communication).

The observed variations in lead isotopes are almost surely due to the mixing of leads with different radiogenic components. Variations due to fractionation during transportation and deposition have been suggested (9) but this remains to be demonstrated.

[1] Lamont Geological Observatory, Palisades, New York, Contribution No. 266.

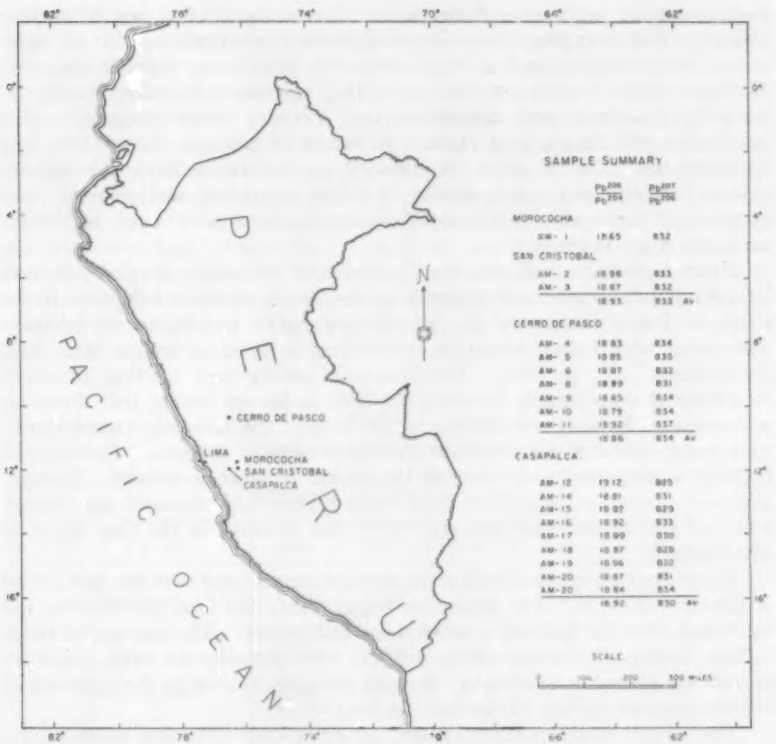

FIG. 1.

The Tertiary Pb-Zn-Cu mineralization of the Peruvian Andes represents an area of special interest with regard to the isotope geology of lead for several reasons: (1) the striking mineralogical zoning of the ore deposits, (2) the great horizontal and vertical extent of the ore and (3) the synchroneity of the ores and major intrusives in the area.

A representative set of galena samples was collected which originates from a variety of hydrothermal deposits in Central Peru (Fig. 1). The major localities are Morococha, San Cristobal, Cerro de Pasco and Casapalca. The lead isotope analysis was done using the lead tetramethyl procedure and the mass spectrometer described by Bate, Miller and Kulp (2).

GEOLOGIC SETTING

McLaughlin (7) has described the regional geology of the Peruvian Cordillera from which the galena samples were collected and this is briefly summarized below. The sampled area is underlain by a thick series of slightly

metamorphosed argillites and sandstones of possible Silurian age (Excelsior series). The overlying Permo-Carboniferous formations consist of sandstone, conglomerates and a thick series of pyroclastic volcanic material. Mesozoic rocks from a sequence of varying thickness, including mainly alternating limestones and sandstones, and Tertiary rocks comprise mostly sandstones and shales, plus various sequences of volcanic flows, tuffs, and agglomerates. The sequence is intruded by numerous stock-like igneous masses varying from quartz diorite to quartz monzonite and granites, with massive or porphyritic textures. No intensive masses of large batholithic proportions are exposed.

From a genetic standpoint the Cerro quartz monzonite porphyry is most interesting. It is generally regarded as the source of the ore deposits in the Cerro de Pasco district but the "genetic association is a matter of inference from other well known examples rather than a direct deduction from local observations" (7, p. 618). Pre-Mesozoic folding and faulting produced structures of considerable intricacy but little is known except that these are widespread. Folding and faulting at the close of the Mesozoic (north-northwest trend) initiated the dominant structural trend of the area. Folding and faulting accompanied and followed the period of igneous activity. Tertiary explosive eruptions broke forth from many centers and blanketed the country with ash and agglomerate material which was involved in the final phase of deformation.

Mineralization is considered to be definitely associated with the last period of intrusive activity. Ore deposition began before the final deformation and continued after the last major movements had ceased. The ore bodies range in type from contact metamorphic deposits with abundant minerals indicative of high temperatures to cinnabar deposits probably related to the solutions of neighboring hot springs (Huancavelica area).

The sample localities cover an area 80 miles long (trending north-south) and represent geologic environments characterized by (1) pronounced mineral and metal zoning over considerable lateral and vertical distances and (2) association of vein and irregular "manto"-type ore occurrences with quartz monzonite intrusives. The *Morococha* sample (No. 1) comes from the fringe of a mineralized area characterized by pronounced mineral zoning (horizontally and vertically) related to a group of Tertiary quartz monzonite intrusions. Ore in the Mesozoic limestones and sandstones occurs as veins and irregular bodies (mantos), the latter type usually at or close to igneous contacts. Mineralization in the related intrusions is dominantly copper while silver and lead appear in increasing amounts (relative to copper) with increasing distance from the intrusions. Zinc is abundantly associated with copper in the intermediate zone and dominant with lead in the outer zone (8, p. 517). The *San Cristobal* specimens are similar in setting, occurring 12 miles south of Morococha along an anticlinal structure common to both areas. The deposit is polymineralic, containing copper-lead-zinc. The two samples are from separate vein systems in the outer zone of mineralization. The ores of the *Cerro de Pasco* district occur principally along the eastern and southern margins of a body of tuff and breccia filling the deeply eroded vent of an

extinct volcano, and along a major zone of faulting separating Mesozoic limestone on the east from the altered Paleozoic sediments, Tertiary tuffs and intrusives on the west. Tabular replacement bodies extend into the limestone roughly parallel to the eastward dipping bedding. Subsequent to intrusion of the Cerro monzonite, sulphide solutions passed upwards along the eastern wall of the vent and produced one of the world's largest pyrite deposits (over one mile long and a maximum width of 1,000 feet). Galena and sphalerite occur in abundance at various points in the massive pyritic body. The true controlling factors for lead-zinc mineralization are unknown. The overall genetic relationships between the different lead-zinc deposits in the Cerro mine have not been established. The seven galena samples from Cerro can therefore be classified only in regard to their depth in the mine and occurrence in irregular shaped bodies. The Casapalca deposit is characterized by the persistence of several main veins laterally (3,300 m) and vertically (1,400 m)

TABLE 1

LEAD ISOTOPE ABUNDANCES OF GALENA SAMPLE

(Average standard error: 206/204 and 207/204 = 0.1, 208/204 = 0.2, 207/206 = .002, 208/206 = .004)

Sample no.	Locality	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}	207/206	208/206
Am-1	Morococha	1.000	18.65	15.52	38.71		
	(La Estaca, Cuña)	1.353	25.23	21.00	52.38	.832	2.076
Am-2	San Cristobal	1.000	18.98	15.81	39.45		
		1.329	25.23	21.01	52.43	.833	2.078
Am-3	San Cristobal	1.000	18.87	15.71	39.12		
		1.339	25.27	21.03	52.38	.832	2.073
Average			18.93	15.76	39.29	.833	2.076
Am-4A	Cerro de Pasco	1.000	18.83	15.69	39.12		
		1.340	25.23	21.03	52.42	.834	2.078
Am-5	Cerro de Pasco	1.000	18.85	15.73	39.05		
		1.340	25.26	21.08	52.33	.835	2.072
Am-6	Cerro de Pasco	1.000	18.87	15.71	39,21		
		1.337	25.23	21.00	52.43	.832	2.078
Am-8	Cerro de Pasco	1.000	18.89	15.70	39.23		
		1.337	25.25	20.99	52.45	.831	2.077
Am-9	Cerro de Pasco	1.000	18.85	15.73	39.11		
		1.339	25.24	21.06	52.37	.834	2.075
Am-10	Cerro de Pasco	1.000	18.79	15.68	38.99		
		1.343	25.24	21.06	52.36	.834	2.074
Am-11	Cerro de Pasco	1.000	18.92	15.83	39.44		
		1.330	25.17	21.06	52.45	.837	2.084
Average			18.86	15.72	39.16	.834	2.077

TABLE 1—*Continued*

Sample no.	Locality	Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}	207/206	208/206
Am-12	Casapalca	1.000	19.12	15.78	39.43		
	Caprichosa	1.328	25.39	20.94	52.36	.825	2.062
Am-14	Casapalca Proper	1.000	18.81	15.64	39.16		
		1.340	25.21	20.96	52.47	.831	2.081
Am-15	Casapalca Proper	1.000	18.82	15.61	39.03		
		1.343	25.28	20.96	52.42	.829	2.074
Am-16	Casapalca Proper	1.000	18.92	15.77	39.16		
		1.336	25.28	21.07	52.32	.833	2.070
Am-17	Casapalca Proper	1.000	18.89	15.68	39.11		
		1.339	25.30	21.00	52.37	.830	2.070
Am-18	Casapalca Proper	1.000	18.97	15.72	39.32		
		1.333	25.29	20.96	52.42	.829	2.073
Am-19	Casapalca Proper	1.000	18.96	15.76	39.27		
		1.334	25.26	21.02	52.39	.832	2.074
Am-20	Casapalca Proper	1.000	18.87	15.68	39.08		
		1.340	25.29	21.01	52.37	.831	2.071
Am-21	Casapalca Rosaura	1.000	18.84	15.72	39.01		
		1.341	25.27	21.08	52.31	.834	2.070
Average			18.92	15.71	39.20	.830	2.072
Average—Entire region			18.88	15.71	39.18	.832	2.075

together with pronounced zoning and telescoping of zones within individual veins. Mineral zones grade from strong alteration and silver in the center to copper-lead-zinc in the intermediate zone, and realgar-stibnite-carbonate gangue at the extremities of the vein system. Table 2 indicates the samples levels in the mine together with the isotope values.

RESULTS

The isotopic analyses of the galena samples are summarized in Table 1. The isotopic abundances are given on the basis of 100 percent and relative to

TABLE 2

VERTICAL DISTRIBUTION OF ISOTOPIC DATA IN THE CASAPALCA MINE

Sample no.	Mine level	206/204	207/204	208/204	207/206
14	1,200′	18.81	15.64	39.16	.831
20	1,200′	18.87	15.68	39.08	.831
15	1,400′	18.82	15.61	39.03	.829
16	1,400′	18.92	15.77	39.16	.833
19	2,100′	18.96	15.76	39.27	.832
17	2,300′	18.89	15.68	39.86	.830
18	2,700′	18.97	15.72	39.32	.829

$Pb^{204} = 1.000$. The ratios 207/206 and 208/206 are also given along with the average value for each deposit. The average standard error for each ratio is given. This is equivalent to the 66 percent confidence level. The standard error is derived from the standard deviation obtained from a standard sample which was analyzed 73 times during the period in which these Peruvian samples were assayed. The Pb^{204} abundance is most uncertain and thus limits the absolute values of 206/204 etc.

The several isotopic ratios are related to different geochemical effects. The 206/204 or 208/204 ratios are most sensitive to the addition of radiogenic lead. The 207/206 and 208/206 ratios are independent of the Pb^{204} measurement. The 207/206 ratio is indicative of the time of extraction of the lead from the source rocks and in some cases may indicate the relative age of mixed leads. The 208/206 ratio is a sensitive indicator of the average U/Th ratio of the source rocks if the source is homogenized prior to transportation to the site of deposition higher in the crust and would detect mixing of the two leads from different U/Th environments.

The vertical distribution of samples in the Casapalca mine is given in Table 2.

TABLE 3

LIST OF LOCATIONS AND DESCRIPTIONS OF SAMPLES

Sample no.	Mine area	Location inside this mining area and description of sample
Am-1	Morococha	La Estaca—Cuña, outside mine in Anticona diorite. Pockets and veins of galena, sphalerite, and barite.
Am-2	San Cristobal	Manto-type ore body in uppermost portion of mine: 170 level, 015 stope, +3d floor, western ore body. Large tabular "phenocrysts" of barite (3 inches long), in a matrix of galena and sphalerite.
Am-3	San Cristobal	San Antonio 470–425 stope. Galena in stringers and pockets in limestone and volcanics.
Am-4	Cerro de Pasco	596 No. 2 stope, 6th floor (500 level), Pb-Zn-ore body; breccia.
Am-5	Cerro de Pasco	12175 No. 5 stope, 6th floor (1,200 level), Pb-Zn-ore body; ?brecciated.
Am-6	Cerro de Pasco	12177 No. 5 stope, 13th floor (1,200 level), Pb-Zn-ore body; ?brecciated.
Am-8	Cerro de Pasco	12278, arch back stope, 3d floor (1,200 level), Pb-Zn-ore body; ?brecciated.
Am-9	Cerro de Pasco	A-102 stope, 2nd floor (A level), Pb-Zn-ore body; disseminated mineralization.
Am-10	Cerro de Pasco	6203 stope, 17th floor (600 level), veins and disseminations.
Am-11	Cerro de Pasco	6203 stope, 17th floor (600 level), veins and disseminations.

TABLE 3—*Continued*

Sample no.	Mine area	Location inside this mining area and description of sample
Am-12	Casapalca	Caprichosa; disseminated copper deposit in andesitic lavas with a few stringers and fractures containing galena, tetrahedrite, sphalerite, barite, etc.
Am-14	Casapalca	C-vein North; 1,200 level. Silicified limestone with Pbs, Zns, $CuFeS_2$, quartz, clay, and carbonates as vein minerals. Massive vein, medium grained.
Am-15	Casapalca	Face of C-vein South; 1,400 level; Galena in altered red beds, with ZnS and pyrite in massive, medium grained vein.
Am-16	Casapalca	C-vein N; 1,400 level. Silicified limestone with Pbs, ZnS, $CuFeS_2$, pyrite, much carbonate, in massive, medium grained vein.
Am-17	Casapalca	23 B 570 stope, 2,300 level. Large cubooctahedral galena crystals with concave crystal surfaces produced by edge growth. Crystals covered open lens-shape fissure, about 3 m high and 10 m long. Little sphalerite and quartz associated with galena.
Am-18	Casapalca	L-25, 2,700 level. Massive coarse grained vein of quartz, pyrite, Pbs and ZnS.
Am-19	Casapalca	21-N-East vein, 2,100 level. Massive, coarse grained ore of ZnS, with PbS, quartz, and some pyrite.
Am-20	Casapalca	12-M-35 vein, 2,100 level. Massive, very coarse grained ore with about equal amounts of ZnS, PbS, $CuFeS_2$ and quartz.
Am-21	Casapalca	Rosaura district (Casapalca outside mine); Medium to fine grained massive galena with little pyrite.

DISCUSSION

The most striking thing about these data is the constancy of the lead isotope abundances. All of the samples from San Cristobal, Cerro de Pasco and Casapalca lie within the standard error of the average for each mine and for the average of the district for all isotope ratios. The Morococha sample also agrees perfectly in the 207/206 and 208/206 ratios but is slightly outside the standard error (lower) from the average 206/204, 207/204 and 208/204 values. This suggests that the Pb^{204} analysis may be slightly high in this ore.

It can be concluded that the isotopic composition is constant to within $\pm 0.5\%$ (the experimental uncertainty) for the entire district. This should be compared to variations up to 13.4 percent in the Southeast Missouri District.

This constancy is particularly remarkable when the extremes of conditions represented by the samples are considered. The distance along strike is 80 miles; the vertical distribution covers at least 400 m (Casapalca). From the mineral assemblage and the iron content of sphalerite in these mines Amstutz (1) suggests that Cerro represents higher temperatures of deposition than the other three localities. The galenas can come from all zones (and presumably all temperatures) from the higher temperature copper zone near the intrusive

outward to the lower temperature lead rich zone. Silver increases along with the lead. Zinc is strongest in the intermediate zone.

The *Morococha* sample was taken from an occurrence outside the mine (La Estaca—Cuña). At *San Cristobal* the samples were far apart and taken in pockets of ore in limestone which is intimately associated with barite. One of these is from very coarse-grained ore. The *Cerro* ore occurs filling breccia, disseminated in the country rock and as distinct veins. At *Casapalca* the samples cover the inner chalcopyrite zone, the main copper-lead-zinc zone and the carbonate-realgar-stibnite periphery. Sample 21 was collected in the Rosaura district, an outlayer of the Casapalca vein system. Sample Am 12 is from a peculiar small porphyry copper deposit in lavas located at Caprichosa. It is not clear whether this is of the same age as the main Casapalca vein system. At Casapalca a wide range in crystal size of the galena is also represented.

Although more detailed study is required, the worldwide survey of the lead isotope composition of galenas suggested that lead ores directly associated with Tertiary intrusives are in general not significantly radiogenic and that they will not show large variations. In the Santa Rita district of New Mexico, where copper, zinc and lead mineralization are associated with quartz monzonite stocks, a study of the sulfur isotopes in various sulfides also showed surprising constancy. All of this suggests that where fractures exist from the source depths directly, the hydrothermal phase can leak out of a volume element of the crust about as fast as it forms during a heating cycle. In this case variations in lead isotope composition of galena may be expected. Conversely, if the volume element is completely homogenized (molten) and some silicate melt is intruded first, then followed by ore depositing solutions, the lead isotope composition should be and is found to be relatively uniform.

The following conclusions are suggested from this study:

1. The lead in the ore deposits of the Cerro de Pasco-Casapalca-Morococha district (80 miles in length) has almost constant isotopic composition within the limits of experimental error (i.e., about ±.5% of the ratios 206/204, 207/204, 208/204). This strongly suggests that the lead, and therefore the other economically important metals, came from a single source. The source was most likely one or several closely related magma chambers.
2. The isotopic composition of the lead is consistent with a Tertiary age of mineralization and a source rock composition similar to average continent crust with regard to U/Pb and Th/Pb.
3. No measurable fractionation of the lead isotopes occurred in this complex mineralization. It is becoming increasingly improbable that such fractionation is ever important in the case of hydrothermal lead mineral formation associated with major intrusives. This is at least for an experimental uncertainty of ±0.5%.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support of the Research Division, Atomic Energy Commission, which made possible the investigation.

D. S. Miller was in charge of the mass spectrometer at the time these measurements were made, P. W. Gast, D. S. Miller and W. R. Eckelmann contributed to the discussion of the data. The samples and field descriptions were provided by the second author. The isotopic analyses were performed in the Geochemistry Laboratory of the Lamont Observatory.

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Economic Geology
Vol. 52, 1957, pp. 923–943

STUDIES OF THE SYSTEM IRON OXIDE–SILICA–WATER AT LOW OXYGEN PARTIAL PRESSURES [1]

S. S. Flaschen and E. F. Osborn

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ABSTRACT

In hydrothermal studies of iron oxide-silica-water mixtures at low partial pressures of oxygen the ferrous silicates, fayalite, greenalite and minnesotaite have been synthesized and their stability relations investigated. Equilibrium relationships among phases in the system FeO-Fe_3O_4-SiO_2-H_2O are discussed in relation to mineral assemblages of Lake Superior iron-formation.

INTRODUCTION

Two of the most abundant oxides in the earth's crust are those of ferrous and ferric iron. Their significance in petrology is even greater than as indicated

[1] Contribution No. 56–61, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania. Experimental data presented in this paper appear as part of the Ph.D. dissertation of S. S. Flaschen, A Hydrothermal Study of the System FeO-SiO_2-H_2O, The Pennsylvania State University, 1953. See also, Flaschen, S. S., and Osborn, E. F., 1953, System FeO-SiO_2-H_2O, abstract, Bull., Geol. Soc. America, v. 64, p. 1423.

by their abundance for they act as recorders of oxygen partial pressure. An indication of the oxygen partial pressure at the time of formation of a mineral may possibly be obtained from ferrous-ferric iron ratios in the mineral provided reasonably close estimates may be made of the temperature and composition of the system at time of crystallization of the mineral. Especially needed at present are laboratory data on systems having these two iron oxides as components, and this requires the use of techniques for estimating and controlling oxygen partial pressures in laboratory experiments made at high temperatures and pressures.

A great step toward making the iron silicates amenable to systematic laboratory study was the classic work of Bowen and Schairer on the system FeO-SiO_2 (1). This break-through in laboratory techniques made possible the subsequent study of the highly important systems CaO-FeO-SiO_2 (2) and MgO-FeO-SiO_2 (3). Later combining the methods of Bowen and Schairer with those of Darken and Gurry (4, 5), other workers were able to obtain systematic data for the systems FeO-Fe_2O_3-SiO_2 (6) and MgO-FeO-Fe_2O_3-SiO_2 (7).

In these previous studies on iron silicate systems the oxide component water is not present. With water as well as iron oxide present new techniques are required because high pressure equipment must be used at the same time that the oxygen partial pressure is controlled. In this paper the writers describe an attempt to obtain some useful information on the synthesis and stability relations of the iron silicates having compositions in the system FeO-Fe_3O_4-SiO_2-H_2O. By maintaining a very low oxygen partial pressure ferrous iron silicates have been synthesized permitting an estimation of phase relationships in the system.

EXPERIMENTAL PROCEDURE

Experiments were carried out in pressure vessels of three types. The most commonly used was a closed autoclave of 4 ml capacity constructed of Type 316 stainless steel, as described by Roy and Osborn (8). The charge of solid starting materials, a few tenths of a gram, was wrapped in platinum foil, placed in the vessel along with a small amount of water, and the vessel sealed and inserted into a controlled temperature furnace for a period of time, usually a few days or weeks. The time allowed was that judged sufficient to attain a close approach to equilibrium among the phases. At the end of the period the vessel was quickly cooled by water or an air blast, and the contents examined. In the lower temperature range, pressure is a function of temperature and was considered to be about that of the vapor pressure of pure water, or for example at 350° the pressure was about 2,400 psi. Above the critical temperature (374° for pure water) pressure is a function of degree of filling of the vessel with water, as well as being dependent on temperature. In this higher temperature range, pressures were estimated using the data of Kennedy (9). Runs could be made up to temperatures of about 500°. The other two types of vessels were connected by pressure tubing to water pumps. In these therefore the water pressure was measured and could be varied independently of

temperature. One of these was a "test tube" type (8), having a bore of $\frac{1}{8}$ inch and made of 18-8 stainless steel, useful to about 750° in these experiments. The other was the "Tuttle" bomb (10), made of stellite No. 21 and suitable for runs up to 925°. Advantages of the latter two types of vessels over the first were: (1) water pressures were independent of temperature and were measured, (2) higher temperatures could be used, and (3) a more rapid quench was possible. Advantages of the first type were: (1) larger charges could be used, and (2) the aqueous phase was enclosed at constant temperature, giving a closed system except for hydrogen loss through the steel walls.

Solid substances were selected for starting materials which were reactive and which at the same time made possible the attainment of an appreciable hydrogen partial pressure. The environment was thus one of very low oxygen partial pressure suitable for synthesizing phases and studying reactions in the system FeO-Fe_3O_4-SiO_2-H_2O. Ferrosilicon alloys were found to be the most satisfactory as starting substances. These reacted with water to give oxide phases plus hydrogen. Alloys of 15, 25, 50 and 75 weight percent silicon were used, ground to pass through a 270 mesh screen. In some runs a mixture of ferrous chloride and ethyl orthosilicate was added to the ferrosilicon alloy. With this "salt" starting material present, reaction was more rapid and crystal size usually larger.

The reaction products in this study were identified and compared with type specimen natural phases by standard petrographic microscope and X-ray diffraction (Fe radiation) techniques. Morphologies of the fine grained hydrous phases were examined with the aid of the electron microscope (RCA model EMU-2D). Temperatures were measured and controlled by chromel-alumel thermocouples inserted in vessel wells immediately adjacent to the sample. Standard potentiometric type equipment was used for temperature control to ± 5° C. Pressures were measured with a Bourdon-type gauge and are probably correct to ± 5%.

SYNTHESIS OF THE CRYSTALLINE PHASES

Fayalite.—The iron olivine fayalite, Fe_2SiO_4, was synthesized readily as large well developed colorless crystals using ferrosilicon alloys as starting materials. The crystals may be synthesized and grown under these hydrothermal conditions from the maximum temperature employed (925°) down to 250°. Below this lower limit hydrous phases appear. The optical properties and X-ray diffraction pattern of the fayalite were very close to those of Rockport fayalite type specimens analyzing less than 1 percent ferric iron. Indices of refraction of the synthetic crystals were: $X = 1.824$, $Y = 1.864$, $Z = 1.879$; $2V = 50°$.

Ferrosilite.—In their studies of the systems FeO-SiO_2 (1) and MgO-FeO-SiO_2 (3), Bowen and Schairer showed that the compound $FeSiO_3$ representing the hypothetical end-member of the pyroxene series does not exist in equilibrium with liquids in these systems. The compound was not synthesized under any conditions used by these investigators, and they concluded that it is not a stable phase at elevated temperatures. Later Bowen (11) dis-

covered and described needles occurring in the lithophysae of obsidian. He judged the needles had a composition very close to $FeSiO_3$. For these crystals he proposed the mineral name "clinoferrosilite." He considered it possible that these crystals are stable at low temperatures.

Sahama and Torgeson (12) treated the problem of the stability of "orthoferrosilite" from a thermodynamic standpoint. The data available permitted only the judgment that orthoferrosilicate is much less stable than is enstatite with respect to the olivine-quartz assemblage. It could still be possible that a ferrosilite is stable at some low temperature.

In our hydrothermal studies no evidence for existence of ferrosilite was found. At temperatures in the range of 480° to the maximum used of 925°, starting materials of the composition $FeO.SiO_2$ yielded only a mixture of fayalite and cristobalite (or quartz). At temperatures below 480° minnesotaite and greenalite formed. It may be that in this low temperature range a ferrosilite crystal is stable, but if true, synthesis will have to be done by other techniques. Bowen's natural clinoferrosilite crystals may have been deposited from the gas phase as metastable structures, or as he suggests there may be sufficient of other metal ions present besides iron to make the crystals a stable phase.

Minnesotaite.—Minnesotaite is a 2 : 1 layer lattice silicate approaching closely in composition to a ferrous iron analogue of the magnesium silicate talc, or $Fe_3Si_4O_{10}(OH)_2$. Based on analysis of the mineral from its type locality, Gruner proposed the formula $(OH)_{22}(Fe'', Mg)_{22.2}.Si_{30.4}(Al, Fe''')_{1.4}O_{74}$ (13). The ferrous iron end member of the talc series was synthesized from both alloy and alloy-salt starting materials below a temperature of 480°. The synthetic phase occurs as colorless needles (positive elongation) and as plates, of which those with minimum interference color exhibit a negative acute bisectrix figure with a $2V < 5°$. Indices of refraction are: $X = 1.586$, $Y = 1.618$, $Z = 1.618$. The optical properties and x-ray characteristics of the synthetic phase correspond closely to those of colorless, low magnesium varieties of the natural mineral analyzing less than 1% ferric iron.

Greenalite.—Greenalite is a member of the serpentine group, a ferrous analogue of antigorite approaching the end member composition $Fe_3Si_2O_5(OH)_4$. Gruner (14) gives the formula of the mineral as $(OH)_{12}Fe_9'' Fe_2'''Si_8O_{22}.2H_2O$ from analysis of typical material. Synthetic greenalite was obtained from both alloy and alloy-salt starting materials at temperatures below 470°. The X-ray powder pattern of this phase corresponds closely to that reported for natural greenalite by Gruner (14). Even at the very low oxygen pressures of these experiments, ferric iron exists in this compound in amounts sufficient to give rise to the pale green coloration characteristic of the natural phase. Because of their fine-grain size and weak birefringence the crystals appear to be isotropic under the light microscope. Index of refraction is 1.67. Under the electron microscope short laths and plates are discernible at 15,000 ×.

Ferro-ferrisilicate Hydrates.—A previous synthesis of greenalite has been reported (15) in the reaction of ferrous chloride and sodium metasilicate solutions at the boiling point in open air. In our preliminary studies these experi-

ments were repeated. In all variations of the basic method the gelatinous products, although resembling greenalite in physical appearance, were found to be amorphous to X-rays. The reaction products in a closed system at 300° consist of acmite, $NaFeSi_2O_6$, and fayalite. In some runs sodium metasilicate was replaced by ethylorthosilicate as the source of silica. The products of this reaction are deeply colored, hydrated ferro-ferrisilicate precipitates exhibiting chlorite and mica type X-ray diffraction characteristics. Under more reducing conditions, obtained by adding H_2 to the water, these reaction products can be replaced with crystalline greenalite.

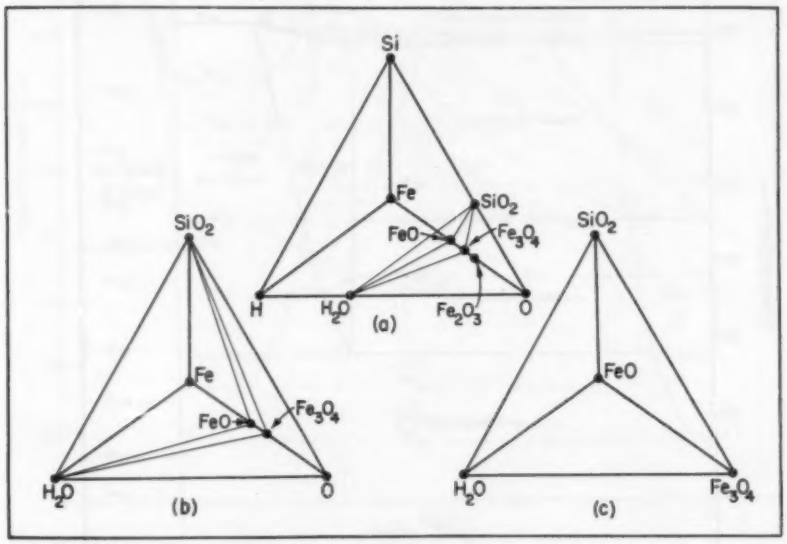

FIG. 1. Diagrams illustrating certain geometrical relationships in the system Fe-Si-O-H. (a) The system portrayed as a tetrahedron with an element at each apex and showing the position of the subsidiary tetrahedron FeO-Fe_3O_4-SiO_2-H_2O. (b) The system Fe-O-SiO_2-H_2O as an equilateral tetrahedron. (c) The system FeO-Fe_3O_4-SiO_2-H_2O as an equilateral tetrahedron.

Grunerite.—Grunerite, the ferrous iron amphibole approaching in composition the formula $Fe_7Si_8O_{22}(OH)_2$, could be obtained synthetically only as an intermediate product in the hydrothermal decomposition of minnesotaite. Ferrosilicon alloys and alloy-salt starting materials in the composition range of grunerite crystallize below 480° C to minnesotaite and fayalite and above 480° to fayalite and silica (Table 1). Associated with fayalite and silica however, in short run decompositions of both synthetic and natural minnesotaite above 480°, are high index, acicular crystals with positive elongation. In runs of 24 hours at the optimum temperature of 700° and 17,500 psi a sufficient amount of this new phase is developed to give an X-ray pattern, found to be identical with that of Rockport grunerite type specimens. In runs of

several days' duration grunerite is replaced completely by fayalite and silica. In mode of synthesis and in stability relationships grunerite thus appears very similar to the magnesium amphibole anthophyllite as described by Bowen and Tuttle (16).

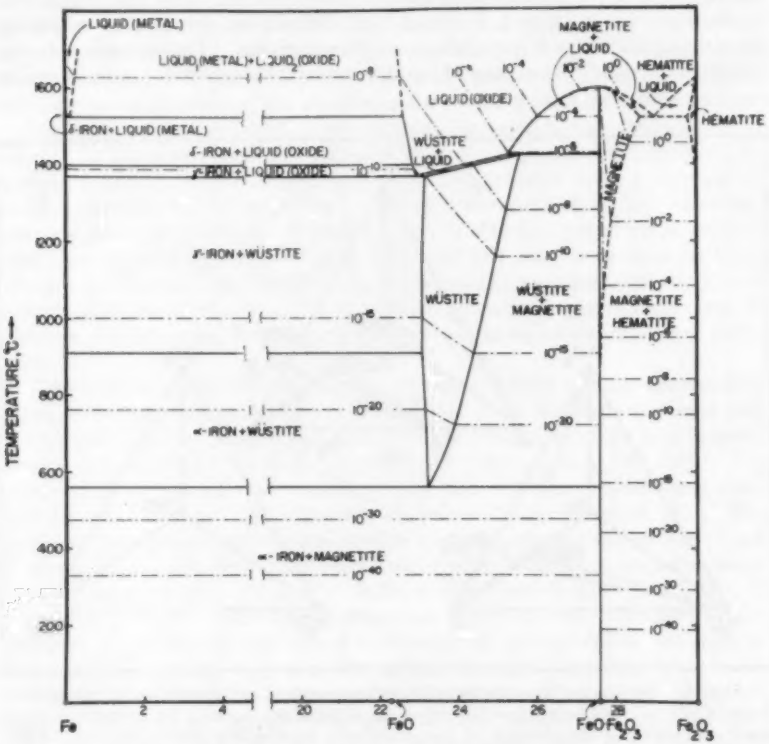

FIG. 2. Phase equilibrium diagram of a part of the system Fe-O, drawn by Muan (17) from data in the literature. Heavy lines are boundary curves between adjacent condensed phase areas, and light dash-dot lines are O_2 isobars in atmospheres. Dashed boundary curves in the upper right hand corner of the figure illustrate inferred probable phase relationships in a part of the system which has not been studied experimentally ($P_{O_2} > 1$ atmosphere).

Wüstite.—The ferrous oxide structure, wüstite, was readily synthesized hydrothermally by reacting metallic iron powder above a minimum temperature of 560° for one hour. In runs below 560° iron oxidized directly to magnetite. These reactions are in conformity with published data as presented in the diagrams of Figures 2, 3, and 4. Although wüstite crystals could be grown only above the minimum temperature of stability of this compound (560°), with rapid cooling of the pressure vessel wüstite crystals persist

metastably to room temperature without dissociation to magnetite and iron and without hydration.

Silica.—Although quartz is presumed to be the stable modification of silica under the temperature and pressure conditions of this study, the high temperature polymorph, cristobalite, was normally obtained in iron-bearing runs.

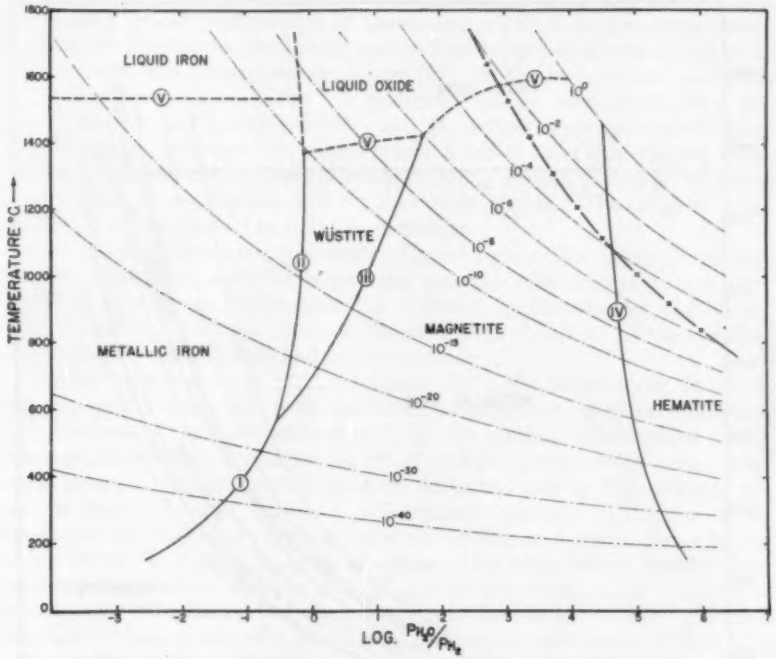

FIG. 3. Diagram illustrating phase equilibrium relationships among iron oxides and iron as a function of temperature and the P_{H_2O}/P_{H_2} ratios of the gas phase. Heavy lines delineate condensed phase areas and series of dashed lines crossing diagram indicate partial pressures of oxygen (in atmospheres). Dash-cross line at upper right represents equilibrium values of P_{H_2O}/P_{H_2} of pure water as a function of temperature (after Muan [2]).

As the time and temperature are increased, quartz is found to replace cristobalite in the reaction product, with runs of ten days or more necessary for complete conversion.

PHASE EQUILIBRIA

General Statement.—The system iron oxide-silica-water is a part of the elementary quaternary system iron-silicon-oxygen-hydrogen. In Figure 1a this quaternary system is represented as a tetrahedron with an element at each

[2] Muan, A., 1957, Personal communication.

apex and with the iron oxides, silica and water shown as compounds located on the edges. The composition volume of particular interest is the subsidiary tetrahedron FeO-Fe_3O_4-SiO_2-H_2O (Figs. 1a, b, c). Crystalline phases studied have compositions which may be represented in terms of these four components, FeO, Fe_3O_4, SiO_2 and H_2O. At the low oxygen partial pressure

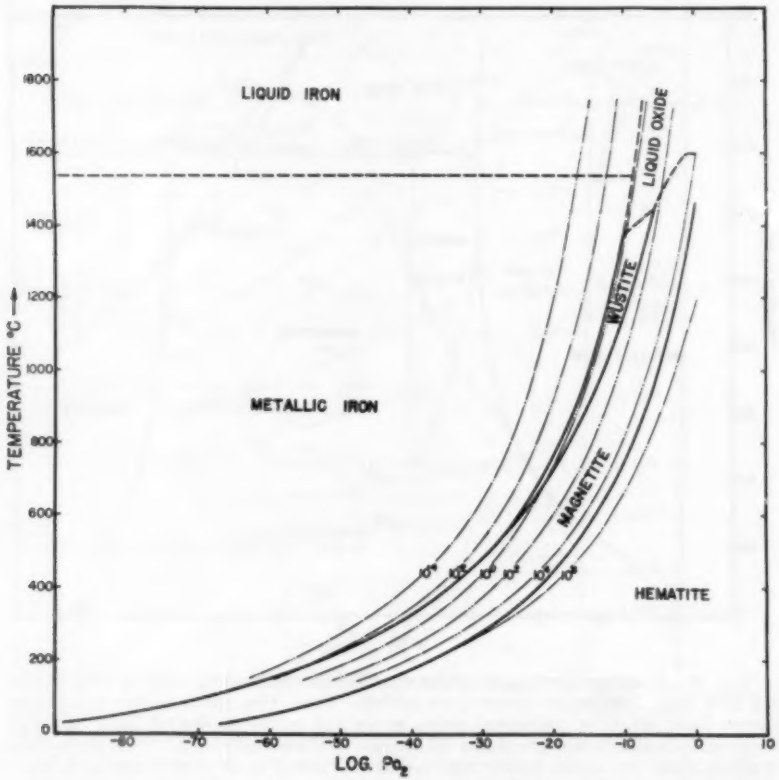

FIG. 4. Diagram derived from Figure 3 by plotting log of the partial pressure of oxygen along horizontal axis with values of P_{H_2O}/P_{H_2} shown as curves (after Muan [3]).

obtaining during the runs, compositions of the crystalline phases lie close to the face FeO-SiO_2-H_2O except that the stable form of the iron oxide itself is Fe_3O_4 rather than FeO. Gases and liquids in equilibrium with these crystalline phases contain excess hydrogen over the 2 : 1 hydrogen-oxygen ratio of water and hence are represented by points lying outside the tetrahedron FeO-Fe_3O_4-SiO_2-H_2O.

[3] Muan, A., 1957, Personal communication.

Data are available from the literature and discussed below, which aid in understanding certain of the phase equilibria on two of the faces of the tetrahedron FeO-Fe_3O_4-SiO_2-H_2O (Fig. 1c). Data for the system Fe-O-H apply to the face FeO-Fe_3O_4-H_2O, and liquidus data exist for the system FeO-Fe_3O_4-SiO_2.

The System Fe-O-H.—A good starting point from which to depart into the complex phase relationships of the system Fe-O-H is the composition-temperature diagram for the binary system iron-oxygen as shown is Figure 2. This diagram was constructed by Muan (17) on the basis of data available in the literature. Compositions of condensed phases were taken from the data of Darken and Gurry (4) (5), and O_2 isobars were constructed from data referred to in connection with Figures 3 and 4. On this diagram compositions of phases can be clearly shown, including oxygen partial pressures of the gas phase in equilibrium with the condensed phases. The range in composition of wüstite should be noted in particular.

The lowest O_2 pressures indicated in Figure 2 have little physical meaning. A more meaningful scale for expressing stability relationships among condensed phases in the Fe-O system is obtained by introducing equilibrium ratios P_{H_2O}/P_{H_2} of the gas phase, as shown in Figs. 3 and 4 [4] (P_{H_2O} and P_{H_2} are partial pressures of H_2O and H_2, respectively).

Curves have not been extended below 150°, the temperature at which hematite is in equilibrium with the alpha monohydrate, goethite ($HFeO_2$) (18), because of the incompleteness of data on stability relationships of the iron oxide hydrates. Temperatures are plotted along the vertical axis. Values of log p_{H_2O}/p_{H_2} are plotted along the horizontal axis in Figure 3 and appear as dashed lines in Figure 4. The partial pressure of oxygen in atmospheres is plotted along the horizontal axis in Figure 4 and is shown by the dashed curves in Figure 3. The boundary curve along which metallic iron coexists in equilibrium with gas plus either wüstite or liquid oxide (curve II), as well as a part of the curve for magnetite, wüstite and gas (curve III), have been derived from published data obtained by direct measurements of H_2O : H_2 ratios of the gas in equilibrium with these phases, as follows. The lower temperature part of curve II (600–1,000°) was constructed from the data of Emmet and Shultz (19) while the upper region (1,200–1,515°) was plotted from the data of Chipman and Marshall (20). The low temperature part of curve III (600–800°) was drawn on the basis of data of Emmets and Shultz (19). The upper part of this curve (1,096–1,388°) was constructed on the basis of data reported by Darken and Gurry (4). The latter authors used CO_2-CO and CO_2-H_2 gas mixtures rather than H_2O-H_2 to study the equilibrium described by this line. Their data have been converted to values of H_2O : H_2 ratios by use of equilibrium data for the reactions

$$CO_2 = CO + 1/2\ O_2$$
$$H_2O = H_2 + 1/2\ O_2$$

as tabulated in a recent publication by Coughlin (21). The liquidus curve (curve V) in Figure 3 as well as that part of the hematite-magnetite boundary

[4] After Muan, A., 1957, Personal communication.

(curve IV) falling between 1,100° and 1,450°, likewise, have been constructed from the data of Darken and Gurry (5) by conversion to $H_2O : H_2$ ratios. No experimental data are available for the boundary curve magnetite-metallic iron (curve I), and the hematite-magnetite boundary curve below 1,100° (curve IV). These parts of the curves have been constructed on the basis of calculated values obtained from the standard free energy data tabulated by

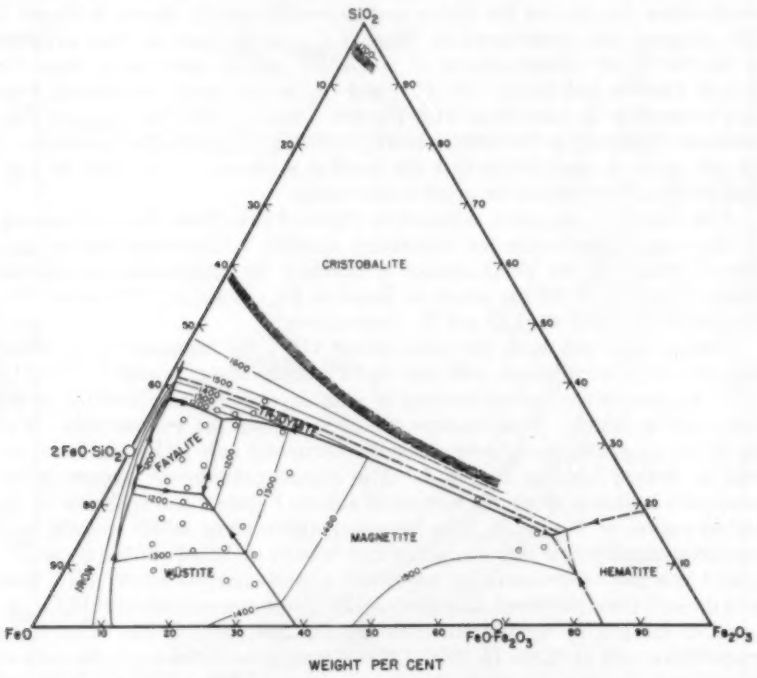

FIG. 5. Phase equilibrium diagram for the system FeO-Fe_2O_3-SiO_2, after Muan (6). Heavy lines are boundary curves, light lines are liquidus isotherms marked in degrees centigrade. Lines with stippling on one side indicate limit of two liquid region at liquidus temperatures.

Coughlin (21). The dash-cross line in the upper right part of the diagram represents equilibrium values of p_{H_2O}/p_{H_2} of pure water as a function of temperature.

The lower limit of stability of wüstite at 560° and the large field occupied by magnetite are features of Figures 2–4 to be particularly noted in connection with the present study. In a hydrothermal system between 560° and the low temperatures at which hydrates are stable (below 150°), magnetite is the stable crystalline phase over the entire area between curves I and IV. Invariably magnetite was therefore the iron oxide phase in our hydrothermal

experiments in the range of 200°–560° inasmuch as metallic iron or iron-silicon alloys were used as part of the starting materials. Reaction of the metal with water to produce oxides lowered the $p_{H_2O} : p_{H_2}$ ratio to the range for stable existence of magnetite. It will be noted however (Fig. 3) that under hydrothermal conditions where the hydrogen partial pressure is limited to that resulting from the dissociation of water ($2H_2O = 2H_2 + O_2$), hematite is the stable phase at temperatures below 1,070°. Hence in an open system

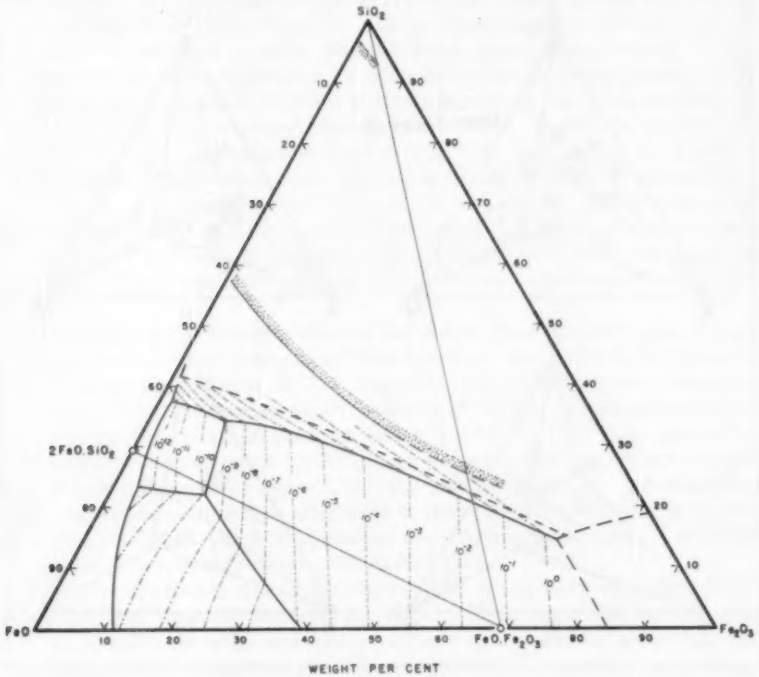

FIG. 6. Diagram of system FeO-Fe_2O_3-SiO_2 showing partial pressure of oxygen in gas phase in equilibrium with condensed phases at liquidus temperatures. Dash-dot lines indicate O_2 pressures in atmospheres (after Muan (6)).

where the hydrogen formed is carried away magnetite can oxidize by the dissociation of water to form hematite or maghemite (or goethite or leipdocrocite may form at low temperatures). In a closed system on the other hand only negligible quantities of the ferric oxide will form from magnetite by the dissociation of water before the oxygen partial pressure is lowered to the point that a magnetite-hematite equilibrium is attained. Hematite was not observed in the reaction products in this investigation.

The System FeO-Fe_3O_4-SiO_2.—Diagrams showing phase equilibrium relationships for the system iron oxide-silica of which FeO-Fe_3O_4-SiO_2 is a part,

are shown as Figures 5 and 6 after Muan (6). Liquidus temperatures and fields for the condensed phases at these temperatures are indicated in Figure 5, while oxygen pressures at liquidus temperatures are shown in Figure 6. It will be noted that both wüstite and fayalite melt incongruently to metallic iron and liquid, as first described by Bowen and Schairer (1) and that no field of stability is shown for $FeSiO_3$. Magnetite is the iron oxide crystalline

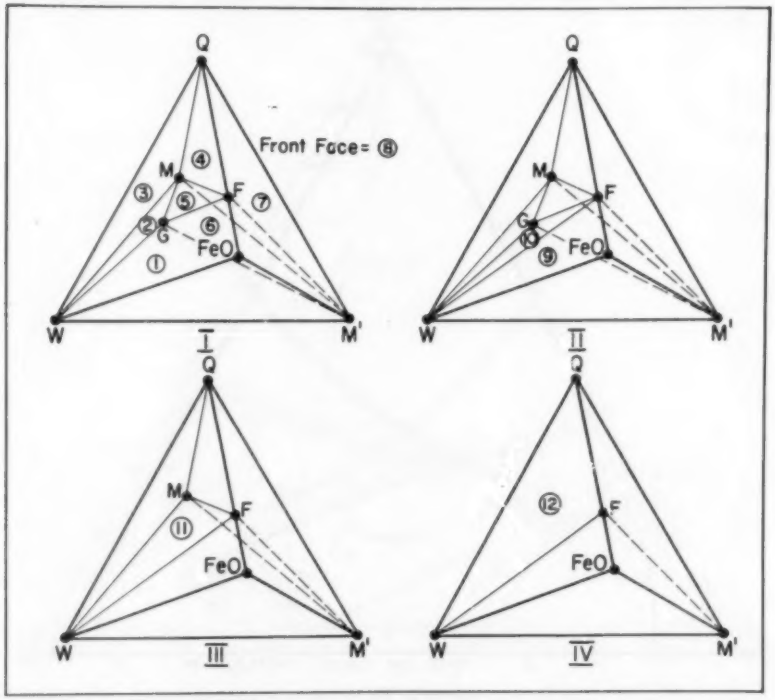

FIG. 7. Series of tetrahedra to show stable phase assemblages in the system FeO-Fe_3O_4-SiO_2-H_2O in four temperature ranges: I = temperatures less than 250° C, II = 250°–470° C, III = 470°–480° C, IV = temperatures greater than 480° C. Circled numbers refer to the different three and four condensed phase assemblages in the system. Abbreviations used: W = water, M′ = magnetite, Q = quartz, F = fayalite, M = minnesotaite, G = greenalite.

structure in equilibrium with liquid over the large range of oxygen pressures from somewhat greater than one atmosphere to a minimum of approximately 10^{-10} atmosphere. As the temperature is decreased below liquidus temperatures, however, hematite becomes the crystalline phase stable over this range of oxygen pressures (Fig. 4). The lower temperature relations between magnetite and hematite can be followed in Figures 3 and 4 where the rapid decrease of P_{O_2} with decreasing temperature along the magnetite-hematite curve

can be seen. At 1,390° the two oxides are in equilibrium in an air atmosphere (0.2 atm. O_2), and at 1,070° they coexist at an O_2 pressure of 10^{-4} atm.

The System FeO-Fe_3O_4-SiO_2-H_2O.—The present study of the system iron oxide-silica-water was made in an environment having a partial pressure of oxygen [5] such that the stable iron oxide phase is magnetite (Fig. 3), and ferrous silicates are stable. This condition was attained by adjusting the alloy-water starting ratios. In this environment in which iron-silicates are predominantly ferrous, compositions of crystalline silicate phases lie close to the plane FeO-SiO_2-H_2O (Fig. 1). As an approximation for purposes of illustration we will also consider that the water phase is represented by the H_2O apex of this plane, although it has a higher hydrogen to oxygen ratio than indicated by the formula H_2O and it contains iron oxide and silica in solution. The system insofar as condensed phases are concerned can then be represented by a tetrahedron having as apices FeO, Fe_3O_4, SiO_2 and H_2O. In Figure 7 four tetrahedra are sketched, each relating to phase equilibrium relationships over a range of temperature and pressure at low oxygen partial pressures. Diagrams are based on data obtained from some 270 runs. Representative runs are listed in Table 1. Varying the water pressure over the range of 2,500 to 17,500 psi was found to have little effect on the temperatures of reactions.

Tetrahedron I is a representation of the stable phase [6] assemblages at temperatures below 250°. It was found that fayalite is not stable in the presence of an aqueous phase below 250°. Magnetite and greenalite were found to coexist and to be the decomposition products of fayalite in this environment. As shown by the apices of triangles in the FeO-SiO_2-H_2O face, greenalite-minnesotaite-water and minnesotaite-quartz-water are other stable assemblages at these low temperatures and low oxygen partial pressures. At somewhat higher oxygen pressures than employed in these experiments, magnetite will be added as a fourth phase to greenalite-minnesotaite-water and to minnesotaite-quartz-water, as indicated by the dashed lines.

Triangles are shown that do not have water as one apex even though experimental data were not obtained for them. These show that fayalite may exist in equilibrium with any one of quartz, minnesotaite, greenalite and magnetite provided an aqueous phase is not present. The possible assemblages are therefore: (1) Magnetite-greenalite-water. (2) Minnesotaite-greenalite-water, with or without magnetite depending on the oxygen partial pressure. (3) Quartz-minnesotaite-water, with or without magnetite. (4) Quartz-minnesotaite-fayalite, again with magnetite added if the oxygen partial pres-

[5] In most of the experiments a gas phase was present, but in many runs below the gas-liquid critical temperature of the aqueous phase (Table 1) water pressures were used which exceed the vapor pressure of water. In these runs where no vapor phase is present, as well as in rocks where the water pressure is greater than the vapor pressure, the term "partial pressure" of O_2, H_2O and H_2 has little meaning as it is ordinarily defined. Here the term "fugacity" would be more appropriate. However, to be consistent and to avoid confusion by introducing other parameters not shown in Figures 3 and 4, partial pressures are used throughout. Where a gas phase is present, partial pressure of a constituent is about equal to fugacity.

[6] Compositions of greenalite and of minnesotaite no doubt vary over a considerable range especially with regard to percent of ferric iron. Points shown are for the pure ferrous end members.

TABLE 1

REPRESENTATIVE DATA OBTAINED IN HYDROTHERMAL RUNS

Temp. (° C)	Pressure (psi H_2O)	Reactants*	Time (days)	Products**
220	17,500	FeSi a.	14	Green + Mag
233	425	Salt a.	5	Green + Mag
235	17,500	Fayalite	14	Green + Mag + Fay
235	2,500	FeSi a.	4	Green + Mag
237	7,500	FeSi a.	7	Green + Mag
247	12,500	FeSi a.	4	Green + Mag
250	7,500	FeSi a.	4	Green + Fay + Mag
250	570	Salt a.	8	Fay + Mag
252	2,500	FeSi a.	5	Fay + Green + Mag
252	17,500	FeSi a.	4	Green + Mag
259	12,500	FeSi a.	5	Fay + Mag
260	17,500	FeSi a.	4	Fay + Mag + (Green)
260	2,500	FeSi a.	5	Fay + Mag
265	7,500	FeSi a.	6	Fay + Mag
277	17,500	FeSi a.	4	Fay + Mag
445	7,500	Salt b.	2	Green + Minn
455	2,500	FeSi b.	14	Green + Fay
460	7,500	FeSi b.	4	Green + Fay
460	17,500	FeSi b.	13	Green + Fay
465	12,500	FeSi b.	13	Green + Fay
465	2,500	Salt c.	4	Minn + Sil
485	17,500	FeSi b.	21	Fay + Sil
500	2,500	FeSi b.	14	Fay + Sil
470	17,500	FeSi c.	3	Fay + Minn
470	17,500	Salt c.	3	Fay + Minn
475	12,500	FeSi c.	14	Fay + Minn + Sil
478	17,500	FeSi c.	5	Fay + Minn
484	2,500	Salt c.	4	Fay + Sil
485	12,500	FeSi c.	4	Fay + Sil
485	12,500	Salt c.	4	Fay + Sil
485	7,500	Salt c.	3	Fay + Sil
495	12,500	FeSi c.	14	Fay + Sil
485	7,500	FeSi c.	3	Fay + Sil
490	2,500	FeSi c.	17	Fay + Sil
500	7,500	Salt c.	4	Fay + Sil
450	12,500	FeSi d.	3	Sil + Minn
500	17,500	Greenalite	14	Fay + Sil
510	12,500	Minnesotaite	12	Fay + Sil

* FeSi a. = Ferrosilicon alloy 15 wt. % Si.
FeSi b. = Ferrosilicon alloy 28 wt. % Si.
FeSi c. = Ferrosilicon alloy 50 wt. % Si.
FeSi d. = Ferrosilicon alloy 75 wt. % Si.
Salt a. = Ferrous chloride—ethylorthosilicate mixture (22 wt. % SiO_2).
Salt b. = Ferrous chloride—ethylorthosilicate mixture (39 wt. % SiO_2).
Salt c. = Ferrous chloride—ethylorthosilicate mixture (62 wt. % SiO_2).

** Mag = Magnetite, Green = Greenalite, Fay = Fayalite, Minn = Minnesotaite, Sil = Silica (Quartz or Cristobalite).

sure is sufficiently high. For the stable existence of this assemblage water is required as a constituent in order that minnesotaite may form, but a separate aqueous phase is not present. (5) Minnesotaite-greenalite-fayalite with or without magnetite. Again of course the water content and iron oxide : silica ratio must be appropriate, the total composition in this case lying in the prism FMGM′. (6) Greenalite-fayalite-magnetite where the iron oxide-silica ratio

is higher than points on GF and there is a water deficiency. (7) Quartz-fayalite-magnetite where no water is present in the system. (8) Magnetite-quartz-water where the oxygen pressure is such that a mixture has a composition represented by a point in the front face of the tetrahedron.

Tetrahedron II (Fig. 6) applies to the temperature range 250° to 470°. At temperatures above 250°, fayalite and magnetite coexist with water at the low oxygen partial pressures used. Assemblages (1) and (6) of tetrahedron I are replaced by: (9) magnetite-fayalite-water, and (10) greenalite-fayalite-water, with or without magnetite. Other assemblages remain the same as in tetrahedron I, Figure 6.

Greenalite decomposes to fayalite, minnesotaite and water at approximately 470°, and minnesotaite decomposes to fayalite, quartz and water about 10° higher. Hence tetrahedron III applies only to the narrow temperature range of 470° to 480°. In this short range the new assemblage (11), minnesotaite-fayalite-water with or without magnetite is stable. Finally assemblage (12), fayalite-quartz-water with or without magnetite, is stable under hydrothermal reducing conditions above 480° (tetrahedron IV).

In the four component system FeO-Fe_3O_4-SiO_2-H_2O the proportion of the two components FeO and Fe_3O_4 in a mixture is a function of the P_{O_2}, or of the $P_{H_2O} : P_{H_2}$ ratio. Let us consider that a particular mixture has a constant content of iron, silica and water but a variable oxygen content. Or referring to Figure 1b the composition of a mixture in terms of these three components may be represented as a point on the Fe-SiO_2-H_2O face. As oxygen is added the composition changes along a line from this point toward the O apex. The line passes through the tetrahedron FeO-Fe_3O_4-SiO_2-H_2O, representing all ratios of FeO:Fe_3O_4 in that segment of the line between the H_2O-FeO-SiO_2 and the H_2O-Fe_3O_4-SiO_2 planes in Figures 1b and 1c. The oxidation state of a mixture, which is a function of oxygen partial pressure if equilibrium exists, thus determines the position of a mixture in the tetrahedron of 1c with respect to its location on a line extending from the H_2O-FeO-SiO_2 to the H_2O-Fe_3O_4-SiO_2 face. Depending on the oxidation level, magnetite may or may not be a phase in most of the assemblages, as noted in the above discussion. The presence or absence of other phases in a mixture of a given iron, silica and water content is also related to a specific range of oxygen partial pressure. In other words, and referring to I of Figure 7, fixing the iron, silica and water content in a mixture fixes the composition as being on a line extending from a point on the W-FeO-Q face toward the front face in the direction of oxygen. Through oxidation or reduction of a mixture assemblages may be changed as the total composition of the mixture moves forward or backward along this line having a constant ratio of $Fe : SiO_2 : H_2O$ but a varying oxygen content. Let us take one example using tetrahedron I, Figure 7 to illustrate this.

Assume that an aggregate contains a high percentage of iron and water, that low oxygen partial pressures obtain (but not sufficient that metallic iron is a phase), that the temperature is about 200° and that equilibrium is maintained among the phases. The assemblage will then consist of greenalite, magnetite and water and the total composition will be represented by a point

on the plane WGM′ in the tetrahedron (assemblage (1), tetrahedron I, Fig. 7). Now if oxygen is progressively added to this mixture a progressive change will occur in the composition of those phases having a variable Fe^{3+} : Fe^{2+} ratio, and a change in the phase assemblage will occur at certain partial pressures of oxygen. The main change at first will be an increase in the Fe^{3+} : Fe^{2+} ratio in greenalite with increasing partial pressure of oxygen. As the oxygen partial pressure reaches the level at which greenalite is saturated with Fe^{3+} under the existing conditions of temperature and H_2O pressure, minnesotaite starts forming. The O_2 pressure remains constant at this stage and the composition of each phase is fixed because there are five phases (greenalite, minnesotaite, magnetite, water and gas) coexisting at the chosen temperature (200°). At this condition of equilibrium greenalite contains its maximal Fe^{3+} content while minnesotaite contains its minimal Fe^{3+} content. The point representing the total composition of the mixture moves continuously through the space WMGM′ to the WMM′ plane as oxygen in the mixture is increased at constant oxygen partial pressure. As this change in total composition takes place, magnetite and minnesotaite increase in amount at the expense of greenalite, and the last trace of greenalite disappears at the WMM′ plane. With the elimination of a phase (greenalite), oxygen partial pressure again increases with the oxygen content of the mixture. Minnesotaite, magnetite and water (plus gas) coexist, with the Fe^{3+} : Fe^{2+} ratio in minnesotaite continuously increasing towards its maximum value. As the oxygen partial pressure corresponding to this limit is reached, minnesotaite in the phase assemblage is replaced by quartz and increasing amounts of magnetite, with oxygen partial pressure remaining constant during the process. As this phase change takes place the point representing total composition of the mixture moves continuously through the tetrahedral space WM′MQ. When the last trace of minnesotaite disappears the total composition is represented by a point in the front face (WM′Q) of the tetrahedron, the mixture now consisting of magnetite, quartz and water. With further oxidation the composition of the mixture moves out of the tetrahedron as hematite appears as a phase. The original mixture of low ferric iron greenalite and magnetite (plus water) has been progressively changed to (1) a high ferric iron greenalite plus magnetite, (2) greenalite plus minnesotaite plus magnetite, (3) minnesotaite plus magnetite, (4) minnesotaite plus quartz plus magnetite, (5) quartz plus magnetite.

This example calls attention to the fact that notable changes in the mineral assemblage of a mixture with a composition in the system FeO-Fe_3O_4-SiO_2-H_2O are brought about by changing the oxygen level (P_{H_2O}/P_{H_2} or P_{O_2}). Further it may be noted from the foregoing that where three crystalline phases coexist (along with water and gas or with only the liquid or gas but at a fixed pressure) compositions of all phases are fixed at a selected temperature. When sufficient laboratory data are available on composition of the crystalline phases as a function of temperature and total composition of the mixture, estimation of temperature and partial pressure of oxygen at time of formation of a mineral assemblage in the system FeO-Fe_3O_4-SiO_2-H_2O may be made from a knowledge of the composition of the crystals.

PHASE ASSEMBLAGES IN IRON-FORMATION OF LAKE SUPERIOR REGION IN LIGHT OF THESE EXPERIMENTAL DATA

Assemblages of the minerals encountered in this study occur on a vast scale in iron-formation of the Lake Superior region. Principally because of their economic importance many investigations have been made describing and explaining these deposits. A detailed study of Lake Superior iron-formation has recently been made by James who in summarizing his conclusions on sedimentary facies defines iron-formation as "a chemical sediment, typically thin-bedded or laminated, containing 15 percent or more iron of sedimentary origin, commonly but not necessarily containing layers of chert" (22). These beds with a high content of iron oxide are also characterized generally by a sufficiently high carbon and sulfur content that conditions of low oxygen partial pressure have prevailed during their metamorphism; or in many beds reducing substances may not have been present but the starting material was a "hydrous silica-ferrous iron gel" deposited in an acid environment (23). Judging by nature of phases present the partial pressure of oxygen was of the same order as that in the present experiments. With burial crystalline phases grew from the poorly organized chemical precipitates. Where the oxides were finely and intimately mixed at the start, undoubtedly the aggregates of crystalline phases forming remained approximately in equilibrium with one another and with the liquid and gas phases as temperature and pressure were increased. Fortunately for geologists reactions accompanying the later decrease in temperature and pressure to that now existing did not wholly obliterate the transformations brought about while temperatures were high.

Geologic data have indicated differences in the degree of metamorphism of iron-formation with the recognition by petrologists of moderate to high-grade metamorphism in some areas in contrast to the generally prevailing low-grade state. Higher grade metamorphism for example is recognized in the eastern section of the Mesabi Range, whereas low grade metamorphism characterizes the western section. The iron silicates in the western Mesabi are principally greenalite, minnesotaite and stilpnomelane, whereas in the eastern section grunerite and fayalite are present as phases.

James (22) subdivides iron-formation into four main types: the sulfide, the carbonate, the oxide and the silicate facies. Neither sulfur nor carbon was added as a component to the system Fe-Si-O-H during our study and hence the data are not of direct application to the first two facies except where they contain significant amounts of silicate and oxide phases. Particularly to the silicate facies, however, and to some extent to the oxide facies the results of the present study may be applied, for these facies approach closely compositions in the system iron oxide-silica-water. In our consideration of these facies let us assume three types of starting conditions, and then on the basis of the data and discussion given in the preceding part of this paper judge what mineral assemblages will develop during metamorphism.

Type I. Starting material was fine grained and intimately mixed. Sufficient water was present during crystallization of the mixture for the existence at all times of an aqueous phase. With these conditions, reaction in iron-

formation is assumed to be sufficiently rapid that a close approach to equilibrium is maintained among the phases as temperature is increased.

As the temperature is raised but not exceeding 250°, assemblages (1), (2), (3) and (8) of Figure 6 would be expected to form, the particular one depending on the ratio of iron to silica and of Fe_2O_3 to FeO in the mixture. These are the stable assemblages over the large range of partial oxygen pressures at which magnetite is the stable iron oxide (Figs. 3 and 4). For a bed having a high Fe : SiO_2 ratio, greenalite and magnetite will be the crystalline phases present at the lowest Fe_2O_3 : FeO ratio possible. This lowest ratio is that for compositions lying on the plane WGM′ of Figure 7, and varies from nearly zero for points near the WG join to nearly one for points near M′. If this bed at another locality has the same Fe : SiO_2 ratio but a greater ferric iron content because reducing conditions are less extreme, minnesotaite may be a member of the assemblage along with greenalite or in place of greenalite if the Fe_2O_3 : FeO ratio is sufficiently high. With a still higher ferric iron content in the bed, quartz will join minnesotaite and magnetite, and at highest Fe_2O_3 : FeO ratios only quartz and magnetite will be present.

A bed having a lower Fe : SiO_2 ratio will be composed only of greenalite and minnesotaite or of just one of these or of minnesotaite and quartz, without magnetite, at low Fe_2O_3 : FeO ratios. On oxidation however, magnetite will join the assemblage as the silicates decrease in amount, and again magnetite and quartz will completely replace the silicates if the Fe_2O_3 : FeO ratio is sufficiently high (reaches the value of one). Assuming a significant variability in ferric : ferrous iron ratio of minnesotaite and of greenalite, a virtually pure minnesotaite or greenalite layer may form over an appreciable range of oxygen partial pressure where the iron oxide content is moderate and the oxygen partial pressure remains too low for separation of a magnetite phase. Thus with low grade metamorphism of iron-formation under conditions of Type I the common assemblages found in the field would be expected on the basis of relations shown in tetrahedron I of Figure 7.

Although we are considering here only compositions within the iron oxide-silica-water system, it may be noted in passing that if significant amounts of other components are present, for example alkalies and alumina, other phases will form. One in particular which is common in low grade metamorphosed iron-formation is stilpnomelane. This mineral will no doubt form along with minnesotaite or even in place of it with appreciable alumina and alkalies present.

As the temperature increases beyond 250° fayalite is stable, making possible the two assemblages (9) and (10) (Fig. 7). With continued increase in temperature greenalite disappears at 470° and minnesotaite at 480°. In view of the common presence of fayalite in some of the more highly metamorphosed sections of iron-formation, for example eastern Mesabi range, we judge that these areas were subjected to temperature exceeding 250°. Conversely the common existence of intimately associated greenalite and magnetite in the less metamorphosed areas (western Mesabi, Gunflint, etc.) is indicative of a temperature maximum of less than 250°.

Fayalite is a stable phase at temperatures below 250° if water is insufficient

to give an aqueous phase. It is believed however that the presence of fayalite in these formations usually if not invariably is the result of high temperature rather than water deficiency as further discussed below.

Type II. Starting material as in Type I but amount of water present was insufficient for the existence of an aqueous phase.

If no aqueous phase is present fayalite may exist stably at low temperatures —less than 250°. Referring to tetrahedron I, Figure 7, assemblages (4), (5), (6) and (7) are possible. The indicated higher grade of metamorphism in areas such as the eastern Mesabi Range where fayalite is a phase might be explained as a result of a low water content at time of formation of these phases rather than a higher temperature. Low water content as the explanation does not however seem probable. The presence of grunerite shows that some water was present. It is unlikely that the eastern part of the Biwabik formation would be deficient in water while abundant water existed in the same beds continuing uninterruptedly to the west. Furthermore the more highly metamorphosed areas are characterized by a coarser-grained texture, and this would hardly be promoted by a deficiency in water content. But the *possibility* of an apparently higher grade of thermal metamorphism because of a lower water content remains.

Type III. Starting material was a coarse, inhomogeneous mixture. In some parts of Lake Superior iron-formation where metamorphism has been slight, metastable mixtures have persisted. Granules of greenalite and hematite for example may appear in close juxtaposition in chert as in a specimen from the Gunflint formation figured by James (22). No doubt part of the reason for existence of this non-equilibrium assemblage is the coarse scale of mixing of the three constituents hematite, greenalite and chert. Reaction among these substances to yield magnetite plus quartz as greenalite or hematite (or both) disappeared would be expected if this mixture had been homogeneous on a fine scale.

SUMMARY AND CONCLUSIONS

The system iron oxide-silica-water has been investigated under conditions of low oxygen partial pressure at high water pressures and at elevated temperatures with emphasis on the range 200° to 600° C. Low partial pressures of oxygen (or low $P_{H_2O} : P_{H_2}$ ratios) were obtained by using iron-silicon alloys in the starting mixtures. The ferrous silicates greenalite and minnesotaite were synthesized and found to be stable phases up to 470° and 480°, respectively, where greenalite dissociates to minnesotaite + fayalite + water and minnesotaite to quartz + fayalite + water. Fayalite is stable to the highest temperature used, 925°, and down to 250°, below which it reacts with water to form greenalite + magnetite. Fayalite persists however as a stable phase to lowest temperatures, dissociating below 250° only to the extent that water is present to form greenalite.

Under the conditions of atmosphere used, mixtures lie essentially in the system FeO-Fe_3O_4-SiO_2-H_2O, which may be viewed as a subsidiary tetrahedron in the diagram representing the system Fe-Si-O-H (Fig. 1). With this repre-

senta ion of the system, twelve regions are demarcated (Fig. 7) each representing a composition field having a particular phase assemblage. The phase assemblage existing in a mixture in the system at equilibrium is a function of temperature and composition where it may be convenient to think of the latter in terms of Fe : SiO_2 ratio, Fe_2O_3-FeO ratio and quantity of water. Total pressure seems to have little effect over rather wide limits. Given a constant Fe : SiO_2 : H_2O ratio and starting with a very low partial pressure of oxygen, by increasing the latter at constant temperature an assemblage may progressively change as for example through the following sequence: magnetite + greenalite, magnetite + greenalite + minnesotaite, magnetite + minnesotaite, magnetite + minnesotaite + quartz, magnetite + quartz (each in equilibrium with an aqueous phase). Each stage represents an increase in oxygen content of the mixture. On the other hand if the total composition of a mixture remains constant including total oxygen, but the temperature is raised, a mixture of Fe : SiO_2 : H_2O ratio similar to that in the preceding example might change in mineral assemblage as follows: magnetite + greenalite (up to 250°), greenalite + fayalite (250°–470°), fayalite + minnesotaite (470°–480°), and fayalite + quartz (above 480°). Finally the total water in a mixture must be considered particularly with respect to the existence or non-existence of an aqueous phase, for the crystalline phases in an assemblage having a particular FeO : Fe_2O_3 : SiO_2 ratio may be quite different in the two cases.

Mineral assemblages in Lake Superior iron-formation are natural occurrences of especial interest in the light of this treatment of the system FeO-Fe_2O_3-SiO_2-H_2O. Assemblages in the eastern Mesabi range containing fayalite are viewed as having been subjected to temperatures exceeding 250° in the presence of an aqueous phase at low partial pressures of oxygen. The regions of low-grade metamorphism were probably not treated to temperatures exceeding 250°. Different mineral assemblages where Fe : SiO_2 ratios and grade of metamorphism are similar reflect differing partial pressures of oxygen existing at the time of metamorphism. In some parts of the iron-formation equilibrium was not attained among the phases, but generally a close approach to equilibrium among crystalline phases and an aqueous phase apparently was reached with the particular combination of minerals in an assemblage being a function of Fe : SiO_2 ratio and partial oxygen pressure. At present we can make only rough estimation of the oxygen partial pressures obtaining during crystallization of an assemblage, but *relative* oxygen partial pressures may be judged using Fe_2O_3 : FeO ratios as a guide and comparing assemblages of similar Fe : SiO_2 ratios and similar temperature-pressure history.

The iron minerals will be of increasing significance as indicators of oxygen partial pressure and of temperature during metamorphism, and possibly of total pressure, as more data are obtained on iron silicate systems. From the preliminary and qualitative studies reported in this paper it is clear that the presence or absence of certain phases (fayalite, minnesotaite, greenalite) gives an indication of temperature range; while the partial pressure of oxygen obtaining during metamorphism may be estimated from a consideration of the minerals present as related to ratios of Fe : SiO_2 and Fe_2O_3 : FeO in the mixture.

ACKNOWLEDGMENTS

The writers wish to acknowledge especially the very helpful advice and criticism of J. W. Greig, M. L. Keith, A. Muan, and R. Roy. This research was partly financed through a research grant from the Geophysics Branch of the Office of Naval Research.

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May 11, 1957

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Economic Geology
Vol. 52, 1957, pp. 944–951

ORIGIN OF THE "MANTO" COPPER DEPOSITS IN LOWER CALIFORNIA, MEXICO

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ABSTRACT

All the previous theories, including hydrothermal solutions of magmatic origin; submarine mud volcanoes; hot springs; supergene enrichment; lateral secretion, on the genesis of the copper deposits of "manto" type in the Lower California, Mexico, lack supporting evidence. They do not accord with field observations, which in many respects suggest that the copper was transported in solution from surrounding highs into the Pliocene seas and deposited with the sediments in the shallow waters or near the shore.

INTRODUCTION

In August 1956 the writer joined one of the excursions of the Twentieth International Geological Congress in Mexico, which took him to the Boleo copper and the Lucifer manganese districts in Lower California, Mexico. There the writer came to recognize that several fundamental arguments in the previous theories do not accord with the field evidence, which fully convinces the writer that the copper deposits are of sedimentary origin rather than magmatic.

Acknowledgments.—The writer acknowledges with thanks the kind invitation to Mexico of Mr. Victor H. Abrams, vice-president of C. T. Takahashi de Mexico, S. A., and ample financial aid of Mr. C. T. Takahashi, president of C. T. Takahashi and Co., Inc., Seattle, Wash., that made it possible to carry on extensive geological investigations for five months. Special thanks is due Dr. Jenaro Gonzalez-Reyna, general secretary of the XX International Geological Congress for recommendation to membership and the privilege of visiting these most interesting mineral deposits in Mexico.

THE BOLEO COPPER DEPOSIT

The district is at Latitude 27°–10′ N, Longitude 112°–30′ W, about 4 km SW of the town of Santa Rosalia on the eastern coast of the long peninsula of Baja (Lower) California, Mexico.

The Early Pliocene formation rests upon an erosion surface on the Miocene Comondu volcanics, consisting of andesite and basaltic flows and sills, tuff, breccia, agglomerate, volcanic conglomerate, and tuffaceous sandstone. The Pliocene consists of basal conglomerate, limestone, and tuff sandstone, in five distinct successive series. The Early Pliocene is unconformably overlain by Middle Pliocene, and in turn by late Pliocene. Flat-lying "manto" deposits of copper minerals lie in the basement of each sedimentary series directly above the conglomerate in the Early Pliocene, but not in the Middle or Late Pliocene. By "Manto" is meant (11) a blanket-like layer or stratified ore body, peculiar to Mexico. The areal extent of the manto deposit is approximately 11 km NW–SE, by 2 km NE–SW. The thickness of the mantos varies from 20 to 100 cm and average 80 cm. The principal ore mineral is finely disseminated chalcocite in the tuff sandstone with subordinate chalcopyrite, bornite, covellite, and native copper. The gangues include montmorillonite, oxides of manganese and iron, gypsum, calcite, chalcedony and jasper. The oxidized copper minerals are silicates and carbonates. Numerous faults of recent date cut the sediments and offset the mantos. The only intrusive rock in the area is a pre-Tertiary quartz-monzonite outcropping in the Lucifer district farther to the north and northwest of the Boleo copper district, and is supposed to underly the Comondu volcanics. No post-Pliocene intrusive rocks are known.

GENESIS AND PROCESS OF ORE DEPOSITION

The origin of the Boleo copper deposits and attendant process of ore deposition have been the subject of controversy and the various opinions and theories that have been advanced will be reviewed briefly.

Tinoco (21) concluded that hydrothermal solutions ascending along the faults in the underlying Miocene volcanics deposited copper with the sediments. There is no evidence to suggest possible pre-mineralization faulting in the Miocene volcanics that acted as feeding channels for the mineral solutions that might have deposited the copper in the Pliocene sediments of the five different horizons.

Martinez Baca and Servin Lacebron (12) suggested that introduction of copper was after the sedimentation. He made no reference to a source of the copper, nor process of deposition.

According to Bouglise and Cumenge (2) the source of copper was hot springs. It seems inconceivable that hot springs should recur during five different periods of sedimentation.

Fuchs (4) considered that the tuffaceous sediments and the enclosed copper and manganese minerals were brought up by submarine mud volcanoes. Since the five manto ore beds are not interconnected with feeding channels or pipes, it would have required mud volcanoes for each horizon of the different periods of sedimentation. If there had been many mud volcanoes, then ejected mud flows from many different vents would have formed tuffaceous mud layers and corresponding copper mantos overlapping or cross-bedded with each other. But no such evidence can be observed.

Saladin (19) thought that the copper was probably brought up by mineral springs and muddy eruptions through fissures in the Comondu volcanics. It is difficult even to imagine how deposition of such regular and extensive copper mantos could have taken place in the horizon of each sedimentary bed of five successive periods.

Posepny (16) made a special reference to the Boleo copper deposit and expressed his view that the repeated periodical precipitation of copper in an open sea basin is impossible. He suggested that copper-bearing thermal solutions ascended through the conglomerates and deposited the copper in the overlying tuffs, after being reduced by organic matter probably present. If the process of deposition of copper in the sediments of five distinctly different periods be considered as being out of question, how was it possible then for the mineral-bearing thermal solution to have deposited the copper not only in a single horizon but also in the other four sedimentary horizons?

Krusch (7) ascribed the intimate occurrence of copper, manganese and cobalt minerals in the Boleo deposit to the action of siliceous hot springs. He refers only to the source of the minerals, with little consideration of the process of deposition.

Weed (23) indicated that hydrothermal solutions ascended, silicified permeable conglomerate, and deposited their load of copper and manganese minerals in the overlying clayey tuff. The conglomerate underlying the ore bed shows no evidence of having been silicified. If it had been silicified, then it would have acted as a barrier to rising copper and manganese solutions, and deposition of the metallic minerals should have taken place along with quartzose gangue below the conglomerate. Judging from his statement of the tuff underlying instead of overlying the conglomerate, he evidently was ignorant of the occurrence of the deposit.

De Launay (3) interprets the Boleo deposit as being the chemical concentration of the decomposed metallic minerals derived from the igneous rocks. Further, he delimits the surface extent of the deposit in the proximity of the igneous rocks, which he considers as the source of the epigenetic ore deposit. He seems to have been influenced by the theory of secondary sulphide enrichment for his interpretation, but it is difficult to know how mineralization could have been formed in five distinct horizons without leaving any trace of gossan above or unoxidized primary sulphides below the secondary sulphide zone.

Touwaide (22) thought that the source of the copper can be traced to copper minerals in the tuff, which were oxidized and leached by connate and ground waters that transported them in solution as sulphates. He assumes that connate and ground waters were sufficiently acidic to have oxidized and leached the copper from the primary sulphide copper minerals in the tuff. The process of oxidation as suggested should have taken place at the surface of each sediment before the next sedimentation. Nowhere in the upper horizon of the tuff is there any gossan or limonite indicating oxidation of pyrite or chalcopyrite and generation of sulphuric acid. Furthermore, if the disseminated fine particles of chalcocite had been deposited by reduction of acidity of descending solutions, then the nuclei would have been preferably

primary chalcopyrite or pyrite. There is no evidence in support of his suggestion.

Bellanger (1) called attention to the presence of small fissures produced by faulting, through which copper- and manganese-bearing solutions traversed and deposited their load. His inference of mineralization through the post-mineralization faults is beyond consideration.

Peña (15) expressed his view that circulating low-temperature mineralizing solutions deposited the copper in the sedimentary series under the cover of impervious clayey tuff. He did not explain the possibility of deposition of copper in the five distinct horizons of sediments. Also he made no reference to the source of the mineralized solution nor courses taken by the ascending solutions. The presence of free carbon in places as much as 3 percent and of silicified or chalcocite-coated wood fragments has been mentioned as being proof of reduction and precipitation of the copper and manganese minerals. The precipitation of dissolved metal in solution should be preceded by reduction of acidity of the solution.

Locke (10) criticizes a copper content of 0.2 percent in the original igneous rock, from which Touwaide claims to have derived the copper by leaching, and advances a theory to explain the genesis of evenly distributed chalcocite grains in the clayey tuff by being deposited by ascending solutions that diffused through the fissures and cross-cutting paths. He seems to have made no reference to the source of the mineralizing solution and neglected to explain the process by which it was possible to form manto deposits in the five distinct horizons of sedimentary series.

A recent report by Dr. Ivan F. Wilson (24) is a most elaborate and comprehensive treatise on the subject. Wilson advocates the theory of ascending hydrothermal solutions of magmatic origin. In order to theorize his conception he reconstructed his ideal section diagram (25) showing protruding Comondu volcanics with a gently sloping erosion surface, upon which lie the Early or Lower Pliocene sedimentary series enclosing the five distinct horizons of ore beds, with corresponding underlying conglomerate. Three prominent faults are indicated in the Comondu volcanics, that terminate at the erosion surface of the Comondu and are supposed to have been of post-Comondu and pre-Boleo sedimentation, though in geological section, plate 3, the faults are indicated initiating in the Pleistocene (Santa Rosalia). Further, one of the three and deepest faults comes up to the erosion surface just below the lowest No. 4 ore bed; the second fault comes up to the erosion surface in contact with the No. 4 tuff and below the No. 3 conglomerate; the third fault comes up to the erosion surface in contact with the tuff between the ore bed No. 3 below and the No. 2 conglomerate above. Some upward pointing arrowheads drawn upon the hanging wall side of each fault, though not indicated whether normal or reversed, are meant to signify the origin of and courses taken by the ascending mineral solutions. Further, the pointed arrows on the No. 1 fault indicate inflow of the mineral solution into the overlying tuff; at the No. 2 fault, into the overlying conglomerate; at the No. 3 fault, into the No. 2 tuff and a little below the No. 2 conglomerate, and overflow of the solutions at each outlet flowed upward along the plane of the Comondu and Boleo contact as indicated

with pointed arrows; the solutions probably breaking through the onrushing current or more likely gained access after cessation of onflow into the tuff beds. He infers that the mineralizing solutions ascended through the conglomerate and were trapped below the impervious clayey tuff and diffused into the clayey tuff above, where the copper was deposited as chalcocite. Thus, it appears that the author's diagram is hypothetical based upon his conception, and does not represent actual data.

All the Pliocene, Lower, Middle, and Upper, and Pleistocene sediments were laid down in the sea upon the eroded surface of the Miocene Comondu volcanics.

All the faults cutting and displacing these sediments and ore mantos are undoubtedly post-sedimentation and mineralization.

Some of these post-mineralization faults might have extended farther down into the underlying Comondu volcanics of Miocene age, but it would be entirely out of question to even consider them as having acted as channels for the mineralizing solutions that might have contributed to the formation of these faulted manto deposits.

Any fissures or dikes or veins or faults formed in the Comondu volcanics after consolidation, or long before the deposition of the Pliocene sediments, would be confined within the volcanics, and they could establish no direct genetic relations to the later sediments of Pliocene and Pleistocene, or to any included ore deposits.

The author suggests that copper-bearing thermal solutions ascended along the faults and fissures very likely formed in the Comondu volcanics by a later intrusive, which is by the way nowhere observable, but inferred to be underlying the Comondu. If so, not only the faults or fissures, but also veins or dikes would have cut the Comondu volcanics and extended into the overlying sediments, in which there might have been formed fissure veins or replacement deposits at the contact with limestones. With this in view the Comondu volcanics should invite exploration for possible larger and richer copper deposits, but no such evidences in support of the above suggestions has been found.

The author considers by ideal diagrams that the copper-bearing solution ascended through the Comondu into the overlying sedimentary series, and deposited copper and manganese in the tuff after diffusing upward through the conglomerate.

It is almost inconceivable that ascending solutions could ever deposit copper and manganese minerals in a definite horizon, or right above the conglomerate bed of the five different sedimentary series, without depositing any copper or manganese in or below the conglomerate or the underlying tuff.

The contact between the eroded surface of the Miocene Comondu volcanics and the later sediments might be regarded as a favorable plane or channel way for post-Pliocene ascending solutions. It would be more plausible to assume that the inferred mineral solutions would have found much easier access to sites of mineral deposition along this extensive contact zone than in the five separated impervious clayey tuff sediments over 200 meters in thickness. No deposit of economic value has been reported from this contact zone in depth,

nor from mineralized fissures or veins branching off from the channel, that might be considered as possible feeders of ore solutions to each of the separated manto ore horizons.

POSSIBLE SOURCE OF COPPER

Touwaide (22) suggested the source of copper in the Comondu volcanics and estimated it at 0.20 percent. Wilson (24), however, called attention to the result of his analysis made of fresh Comondu volcanics, which showed only 0.007 percent of copper. He also referred to the average value of 0.018 percent of copper obtained from 169 analyses of igneous rocks.

Since any copper mineral cannot be considered as one of the rock-forming constituents of igneous rocks, variable amounts of copper in the Comondu volcanics or in the tuff or in any other igneous rocks should have no direct bearing on the present discussion.

It is a recognized fact that the abundance of copper in igneous rocks is highest in basic and is lowest in acidic rocks (17). Examples of native copper, chalcocite, and bornite with epidote, calcite and zeolites in extensive distribution in Precambrian basalts in the Lake Superior region are well known (8), and native copper, chalcocite and bornite, malachite and azurite in vesicular and porphyritic andesite in Asturia, on the west coast of Cebu island in the Philippines (13), and native copper, malachite, azurite, and chalcocite in porphyritic andesite in an old mine, 6 km north of San Miguel, Jalisco, Mexico (14), seem to suggest strongly the possible occurrence of primary copper mineral deposits in the andesitic and latitic Comondu volcanics near the surface before the Pliocene denudation.

On the other hand the source of copper may not necessarily be confined to the Comondu volcanics alone. The pre-Tertiary igneous rocks, preferably extrusive, of surrounding highs may have supplied not only copper but also other metallic or nonmetallic elements in solution or in fine detritus to the Pliocene seas.

The cycle of copper is fully treated geochemically by Rankama (18). The weathering of primary copper-iron sulphides, such as chalcopyrite and bornite, decomposes them and the metals go into solution as copper sulphate and ferrous sulphate, the latter being quickly oxidized to sulphuric acid and ferric hydroxide, whereas copper sulphate either migrates downward or is washed into stream. From nearby land areas the copper minerals in part might possibly be transported in fine detritus, as well as in solution, and become deposited with the sediments. If the cupric sulphate solution is brought into contact in shallow waters with sapropelic muds, copper is reduced and precipitated as sulphide, and under favorable depositional environment the formation of extensive sedimentary copper ores is possible.

Thus sedimentary copper deposits are characterized (9) by 1) absence of igneous rocks nearby, or if present, are older than the copper deposits, 2) the sedimentary copper ore strata are of terrigenous or shallow water beds, 3) the principal mineral is chalcocite replacing carbonaceous or calcareous materials with subordinate chalcopyrite and bornite, and 4) gangue minerals consist in general of calcite, gypsum, and barite with a little quartz.

One of the best examples of a copper deposit claimed to be of sedimentary origin is the Kupferschiefer of Mansfeld, Germany (20), which is included in a series of upper Permian sediments consisting in ascending order of basal conglomerate, carbonaceous and calcareous shale with finely disseminated copper sulphides, limestone, gypsum and salt. This typifies a favorable geochemical environment, under which the deposition of copper is considered to have been possible with muddy sediments in shallow seas.

SUMMARY AND CONCLUSION

All the previous theories, especially the hydrothermal solutions of magmatic origin, do not seem to apply to the genesis of the Boleo copper deposits.

The five copper manto deposits are all confined within the sediments; they terminate at the contact with the Miocene Comondu volcanics; they are each independent and are not interconnected.

It is rather far-fetched for those who support an igneous origin to suggest a post-Pliocene igneous intrusive that broke through the Comondu volcanics and introduced copper minerals into the overlying Lower Pliocene sediments through faults that cut the Pliocene and offset the bedded ore.

Thus far no arguments based upon the theory of hydrothermal solutions seem to be applicable to explain the process of deposition of the Boleo copper manto deposits.

As to the source of copper, any andesitic or basaltic extrusives, including the andesitic and latitic Miocene Comondu volcanics, of pre-Pliocene may have possibly supplied the copper through weathering of copper-iron sulphides of near-surface occurrence. The copper could have been transported in fine detritus or in solution as a sulphate with tuffaceous detritus to the shallow Pliocene seas. Reduction, precipitation, concentration, and deposition of the copper as sulphides was probably effected on the carbonaceous, calcareous, gypsiferous and muddy floor of the subsiding coastal plain. Intimate association of the copper minerals with the manganese oxide is another indication of deposition in shallow waters and is suggestive of having close genetic relation with the adjacent Lucifer manganese deposits occurring in the same Pliocene sedimentary formations.

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June 10, 1957

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Economic Geology
Vol. 52, 1957, pp. 952–971

ZIRCONS FROM THE ANIMAS STOCK AND ASSOCIATED ROCKS, NEW MEXICO

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ABSTRACT

Zircons have been studied by measurement of lengths and widths of 200 crystals for each sample. Data are analyzed by the reduced major axis method. Ten samples from the Animas stock, emplaced at shallow depth, have zircons with like reduced major axes. A sample from an apophysis, one from a roof protruberance, and one from near the center of the stock have somewhat different zircon reduced major axes. Contrasting bands in fine- and coarse-grained layered units have zircons with like reduced major axes. The size of zircons varies considerably throughout the stock. Results are compared with those obtained for the Bald Mountain batholith, Oregon, which has been emplaced at moderate depth.

Three samples of tuff that originated from the site of the stock, and two samples from a related, nearby vent have zircons with reduced major axes like those of the zircons of the Animas stock. One tuff sample has a somewhat different zircon reduced major axis than that of the Animas stock. Three granitic xenoliths and a younger extrusive have zircon reduced major axes unlike that of the stock. Five different granitic intrusives also have zircons with different reduced major axes. One different granite has the same zircon reduced major axis as that of the Animas stock, but the zircons differ in other respects.

It is concluded that zircons may be used to characterize granitic rocks of igneous origin and to distinguish derivatives of one magma from those of older or younger magmas, even if the rocks are of identical chemical and mineralogical composition.

INTRODUCTION

THE significance of morphological characters of zircons in sedimentary and igneous rocks has been reviewed by Poldervaart (5, 6). Zircon crops prepared from these rocks may be typed by grain counts at regularly spaced intervals, noting such characteristics as color, zoning, crystal habit, rounding of crystal edges and terminations, inclusions, outgrowths, overgrowths, etc.

This approach, though useful, is only semi-quantitative and not entirely free from subjective bias and judgment. Comparison between samples is even more a matter of personal judgment. Karakida (3) has shown that, nonetheless, encouraging results may be obtained by these methods.

Poldervaart has attempted to overcome these handicaps by measurement of lengths and widths of an adequate sample of grains (200) in zircon crops. In silicic and intermediate rocks of magmatic origin the length of zircons is measured along the *c*-axis, the width along the a_1- or a_2-axis. At first results have been represented graphically by frequency curves of length, width, and elongation (length/width). This treatment yields much useful information, but comparison between samples remains a matter of judgment.

Recently (Larsen and Poldervaart, in press) the method of the reduced major axis has been adopted for the digestion and graphic representation of the 200 measurements of lengths and widths obtained for each zircon sample. The method has been described by Imbrie (2), especially in regard to its application to paleontological problems. Larsen and Poldervaart (in press) have given further details of the application of the method to problems involving zircons in rocks. The reduced major axis of a zircon sample of an igneous rock closely approaches the growth trend of the zircon crystals. The method has the further advantage of allowing rigid mathematical comparisons between samples. Larsen and Poldervaart have also described procedures used in preparing zircon crops for measurement, and have reported results of a series of tests of their methods.

By applying the method of the reduced major axis, Taubeneck (7) has shown that in a granitic batholith at Bald Mountain, Oregon, zircon crops of different rock samples have the same reduced major axes. The uniformity of zircons throughout the batholith is the more striking because the samples; (1) were from localities up to 15 miles apart, (2) were from different elevations, varying as much as 2,000 feet, (3) included contact phases as well as more centrally located rocks, and (4) varied in composition from tonalite with little or no potash feldspar, to granodiorite with up to 14 percent potash feldspar. These results may be expected if the batholith is of magmatic origin and if zircon has crystallized very early in the crystallization sequence of the magma, i.e., before magmatic differentiation. Taubeneck has given independent proof of the magmatic origin of the batholith in his detailed field- and laboratory studies. Further evidence for the early crystallization of zircon in granitic rocks of magmatic origin has been cited by Larsen and Poldervaart (in press).

The Bald Mountain batholith has been emplaced at moderate depths. It has occurred to the writers that study of zircons of a granitic intrusive emplaced at shallow depths would contribute further toward the problem of zircons in granitic rocks. For this study they have chosen the Tertiary Animas stock; an irregular, funnel-shaped intrusive of quartz monzonite-porphyry located in the Animas Range in the north-central part of the Walnut Wells quadrangle, Hidalgo County, New Mexico (Fig. 1).

The Animas stock is about 4 miles long and varies in width from less than ¼ mile to over 2½ miles. Relief within the outcrop area varies by nearly

1,700 feet, elevations being 4,825 to 6,500 feet. The igneous rock contains phenocrysts of potash feldspar, plagioclase, quartz, and biotite, set in a fine-grained groundmass. Relative proportions of phenocrysts and groundmass may vary from 75 percent phenocrysts to 85 percent groundmass. In many places, especially near contacts, the igneous rocks are banded. In the banded rocks coarse-grained, porphyritic material with little groundmass alternates with fine-grained rocks poor in phenocrysts. Outcrops of these banded rocks are generally less than 20 feet wide, but may reach 50 feet in width. The

FIG. 1. Index map of the Walnut Wells quadrangle, New Mexico.

bands dip toward the core of the intrusive and are commonly drag-folded. The Animas stock has sharp contacts and contains relatively few xenoliths of quartz latite, andesite, sandstone, skarn, schist, or granite.

The intrusive is surrounded and partly roofed by the Oak Creek quartz latite tuff. Field- and laboratory studies indicate that the Animas stock has also served as source for the extrusives, although the Oak Creek quartz latite is slightly earlier than the intrusive quartz monzonite-porphyry. A monzonite vent 6 miles south of the Animas stock, the Walnut Wells vent, is also believed

to be penecontemporaneous and derived from the same magma as the quartz monzonite-porphyry of the Animas intrusive.

A detailed geologic report of the Walnut Wells quadrangle will be published elsewhere (Alper, in preparation). This paper reports only the results of the zircon work.

LABORATORY PROCEDURE

Since Larsen and Poldervaart (in press) have described laboratory procedures in detail, only a short summary of the methods used is given here.

The rock samples were crushed to pass through a U. S. Standard 60-mesh screen. Heavy residues were prepared by centrifuging the crushes with bromoform. Magnetic minerals were removed by passing the residues through a Frantz isodynamic separator. The entire non-magnetic residue of each sample was permanently mounted on as many slides as necessary. Traverses were made with a Chayes point counter and spaced so as to cover all the slides in measuring a total of 200 zircons. Measurements were made under high magnification (×270) with an ocular micrometer.

Statistics calculated from the measurements for the reduced major axis are:

$\bar{x}$: mean length — s_x: standard deviation of length
$\bar{y}$: mean width — s_y: standard deviation of width
r: coefficient of correlation

In a plot of length *versus* width the reduced major axis of a zircon sample is drawn through the point $(\bar{x}, \bar{y})$ at an angle, the tangent a of which equals s_y/s_x. The length of the line is determined by omitting 2½ percent each of the longest and shortest crystals measured. If the reduced major axis is regarded as the crystal growth trend, the length of the line has significance only in marking the growth development reached by the sample.

Since the sample is large (200), z tests can be used in comparing reduced major axes of different samples. The level of confidence has been arbitrarily taken at $z \geqslant 1.96$ (probability $p \leqslant 0.05$). Slopes of reduced major axes are compared by first calculating the standard error of slope for each sample:

$$\sigma_a = a\sqrt{\frac{1 - r^2}{N}}$$

after which z is calculated for two slopes:

$$z = \frac{a_1 - a_2}{\sqrt{\sigma_{a_1}{}^2 + \sigma_{a_2}{}^2}}.$$

Positions of reduced major axes are compared by first calculating b, the intercept of each reduced major axis with the y-axis:

$$y = ax + b$$

after which z is calculated for two positions:

$$z = \frac{x_0(a_1 - a_2) + (b_1 - b_2)}{\sqrt{\sigma_{a_1}{}^2(x_0 - \bar{x}_1)^2 + \sigma_{a_2}{}^2(x_0 - \bar{x}_2)^2}}.$$

This tests the hypothesis that, when $x_1 = x_2 = x_0$, $y_1 - y_2 = 0$, i.e., the true growth trends coincide (Imbrie, 1956, p. 237–238). In this study the value for x_0 has been taken arbitrarily at 0.42.

TABLE 1

REPRODUCIBILITY OF ZIRCON MEASUREMENTS

Index	$\bar{x}$ (mm)	$\bar{y}$ (mm)	s_x (mm)	s_y (mm)	a	r	Slopes compared z	Positions compared z	$\bar{x}$ compared z	$\bar{y}$ compared z
A	0.1345	0.0602	0.0555	0.0205	0.3694	0.7883	0.474	0.122	*2.220*	*3.634*
A^{II}	0.1458	0.0670	0.0499	0.0199	0.3804	0.7821				
B	0.1458	0.0703	0.0498	0.0167	0.3357	0.5788	0.678	0.352	0.020	1.178
B^{II}	0.1457	0.0683	0.0484	0.0172	0.3554	0.5052				

Index:

A. Zircons of quartz monzonite-porphyry, Hanover, New Mexico (C-7), separated and measured by L. H. Larsen.

A^{II}. Zircons of quartz monzonite-porphyry, Hanover, New Mexico (C-7), separated and measured by A. M. Alper.

B. Zircons of quartz monzonite-porphyry, Animas stock, New Mexico (6), separated and measured by A. M. Alper.

B^{II}. Zircons of quartz monzonite-porphyry, Animas stock, New Mexico (6), separated and measured by A. M. Alper.

If desired, $\bar{x}$ and $\bar{y}$ of different samples may also be compared, using similar formulae in which x and y are interchangeable:

$$\sigma_{\bar{x}} = \frac{s_x}{\sqrt{N}}$$

$$z = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\sigma_{\bar{x}_1}{}^2 + \sigma_{\bar{x}_2}{}^2}}.$$

The essential elements of the reduced major axis are slope and position. Immature and adult populations may have different sizes, but the same growth trends. Comparisons of $\bar{x}$ and $\bar{y}$ of different samples are therefore not material to the method of the reduced major axis.

Much information is gained by visual inspection of the plots of reduced major axes, even without statistical comparisons. Although in this paper z values are given in all cases, calculation of z is really only necessary in examples where there may be doubt as to similarity or dissimilarity of two or more reduced major axes. If a z test for slopes shows significant differences ($z \geqslant 1.96$), a z test for positions is superfluous.

Reproducibility of the data has been tested for two rock samples; one

of which (C-7) was prepared and measured by two different observers. In each case the entire procedure of crushing, separation, mounting, and measurement was repeated afresh for two pieces of the same rock sample. In the case of specimen C-7 (A and A[11]) the two observers also used somewhat different methods of crushing and separation of the zircon concentrate.

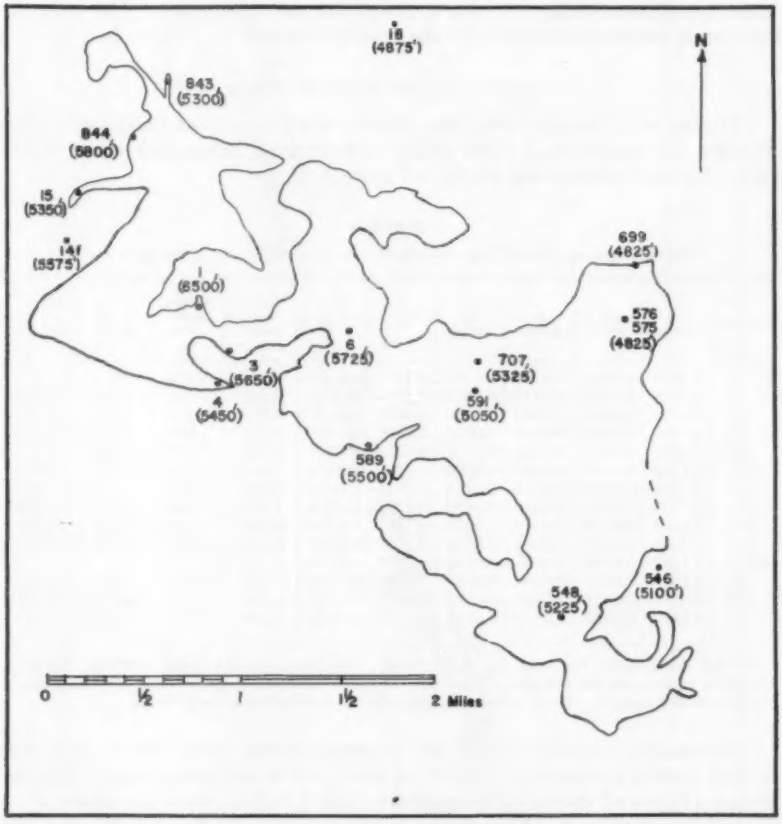

FIG. 2. Map of the Animas quartz monzonite-porphyry stock, Walnut Wells quadrangle, New Mexico. Sample locations indicated by dots, numbers are code numbers, numbers in parentheses are elevations.

Results are given in Table 1. There are no significant differences in the reduced major axes. However, the mean length and mean width are significantly different in the first example, reflecting differences in laboratory procedure; coarse crushing and separation in a separatory funnel for A, and fine crushing and separation in a centrifuge for A[11].

Larsen and Poldervaart (in press) have cautioned that the method of the reduced major axis as applied to zircon studies is not a panacea, but that in many cases treatment of data by this method will need to be augmented by other means of representation of the data (tabulations, frequency curves, or contoured scatter diagrams) and by other observations (habit and color of crystals, type of inclusions, outgrowths, etc.), to bring out and trace specific morphological characters of the zircon samples. The need for caution is also demonstrated by the results obtained in this study.

ZIRCONS OF THE ANIMAS STOCK

Zircons of 13 samples from the Animas stock have been measured. The samples are maximum 3 miles apart, with vertical separations up to 1,700 feet. Sample locations are shown in Figure 2.

TABLE 2

PARAMETERS OF ZIRCON SAMPLES FROM THE ANIMAS STOCK, NEW MEXICO*

Index	$\bar{x}$ (mm)	$\bar{y}$ (mm)	s_x (mm)	s_y (mm)	a	r	Slopes compared s	Positions compared s	$\bar{x}$ compared s	$\bar{y}$ compared s
1	0.1357	0.0679	0.0546	0.0193	0.3543	0.5303	0.814	0.336	1.638	*3.779*
3	0.1126	0.0563	0.0531	0.0209	0.3940	0.7229	0.541	0.690	*2.698*	*2.060*
4	0.1174	0.0595	0.0536	0.0219	0.4080	0.6422	0.964	1.252	1.785	0.476
6	0.1458	0.0703	0.0499	0.0167	0.3357	0.5788	1.503	1.120	*3.684*	*5.337*
548	0.1199	0.0602	0.0455	0.0184	0.4034	0.6558	0.825	1.093	1.419	0.157
575	0.1344	0.0579	0.0585	0.0204	0.3480	0.5978	1.062	1.712	1.346	1.294
576	0.1489	0.0638	0.0711	0.0254	0.3577	0.6632	0.740	1.342	*3.514*	1.447
591	0.1138	0.0565	0.0413	0.0180	0.4373	0.6274	1.836	*1.964*	*2.763*	*2.109*
707	0.1603	0.0728	0.0563	0.0218	0.3862	0.5416	0.244	0.175	*6.117*	*5.910*
844	0.0798	0.0400	0.0364	0.0131	0.3613	0.6288	0.599	0.952	*10.397*	*12.187*
MGT_1	0.1269	0.0605	0.0520	0.0196	0.3786	0.6189				
15	0.1065	0.0504	0.0503	0.0167	0.3316	0.6291	1.688	*2.376*	*3.953*	*5.510*
589	0.0810	0.0438	0.0344	0.0161	0.4677	0.7155	*2.856*	*3.517*	*10.291*	*9.246*
843	0.1349	0.0645	0.0512	0.0178	0.3483	0.6686	1.084	0.954	1.538	*2.119*

* First ten samples are from the main stock. The mean growth trend (MGT_1) has been calculated from these ten samples. Last three samples are from apophyses and a protuberance in the roof of the stock. Each sample is compared with the mean growth trend.

Microscopic examination of the mounted zircon crops shows that the crystals exhibit a remarkable variety of habits, sizes, and elongations. Highly faceted zircons of moderate elongations (1/b 1.5–3.0), with the shape of a football, are abundant. Elongated prismatic crystals (1/b 3.0–7.0) of much simpler habit are less abundant but more conspicuous. Nearly all the crystals are sharply euhedral, while less than 5 percent show slight to moderate rounding of crystal edges and terminations, or have pitted or scarred surfaces. Colorless zircons predominate over yellow or pale brown crystals. Less than 20 percent of the crystals have a broken appearance. Larsen and Poldervaart (in press) have shown that these imperfect crystals are most probably present in the rock and have not been broken by crushing. A few crystals enclose minute zircons, less than 0.03 mm long by 0.015 mm wide. More conspicuous

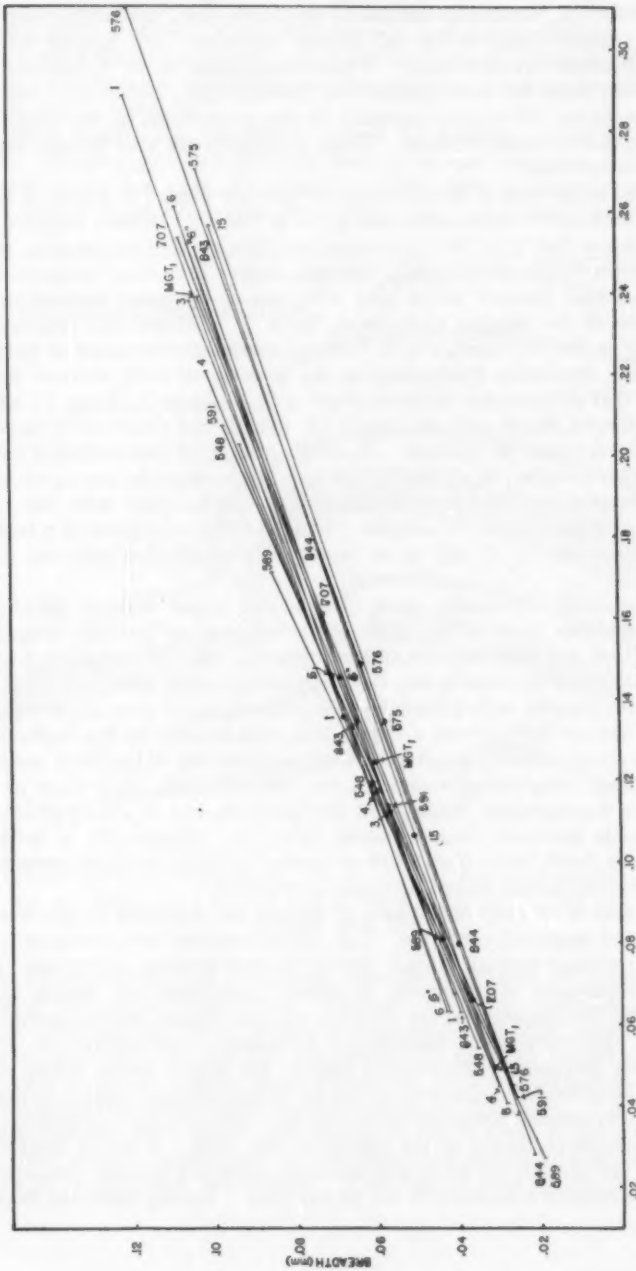

FIG. 3. Reduced major axes of zircon samples from the Animas stock.

are honey brown, vermicular inclusions of unidentified, apparently isotropic material. Apatite outgrowths on zircons are rare, and apatite needles enclosed by zircon are even rarer. Visual comparison of the 13 concentrates indicates that there are many similarities (habits, color, inclusions), but also some conspicuous differences, especially in the proportions of the larger and more elongated prismatic zircons. These differences are also brought out by the quantitative data.

Reduced major axes of the 13 zircon samples are plotted in Figure 3, while statistical parameters and z values are given in Table 2. Visual inspection of Figure 3 shows that 12 of the 13 samples have like reduced major axes, while that of sample 589 has a distinctly different slope. Statistical comparison of the slope of each reduced major axis with that of the mean reduced major axis for ten of the samples (column 8, Table 2) confirms this impression; sample 589 is the only sample with a significantly different slope of reduced major axis. Statistical comparison of the position of each reduced major axis with that of the mean reduced major axis (column 9, Table 2) shows that the reduced major axis of sample 15, though not different in slope, is significantly different in position. However, sample 15 has definite affinities with the other samples; its reduced major axis is, for example, not significantly different in position from that of sample 575 which agrees with the mean reduced major axis for the 10 samples. Sample 591 is even more of a borderline case than sample 15 and again shows definite affinities with the other samples.

The remaining 10 samples have like reduced major axes at the chosen level of confidence ($p \leqslant 0.05$). Five of the samples are centrally located in the stock, four are near contacts of the intrusive, and one sample is from a small apophysis which extends into the surrounding quartz latite tuff (Fig. 2).

The three samples with different zircon reduced major axes are of especial interest. Sample 589 is from a cupola-like protuberance in the roof of the stock. Its zircon reduced major axis is steeper than that of the other samples, indicating that elongations of crystals are somewhat less than those of the other zircon concentrates. Sample 15 is toward the end of a long apophysis which extends westward from the stock (Fig. 2). Sample 591 is centrally located in the stock, but is from a low elevation, hence its actual distance from the contact of the funnel-shaped intrusive is unknown.

Differences in reduced major axes of zircons are attributed by the writers to sorting and magmatic corrosion. All the concentrates have the same types of zircons; mainly football-shaped, highly faceted crystals with minor and varying proportions of elongated, prismatic individuals of simple habit. Zircons of all the concentrates are colorless and have honey brown, vermicular inclusions. However, some concentrates have smaller proportions of larger and of more elongated crystals than others; are simply better sorted than others. The porphyritic character of the rocks indicates that quartz, feldspar, and biotite crystallized intratellurically and were present in considerable proportions upon emplacement of the magma in the stock. It seems likely that zircon also had crystallized before emplacement, especially because thin sections show that zircons are enclosed in the phenocrysts. During turbulent flow of

such a crystal mush with accompanying melt, sorting of prismatic zircons seems a likely process. Magmatic corrosion is also not ruled out as a factor in producing differences in zircon reduced major axes. Sample 589 contains a higher proportion of scarred zircons than the other concentrates and this may well be due to corrosion.

Zircon studies also contribute toward the problem of banding in these rocks. Samples 575 and 576 are from a banded sequence which shows primary drag-folds (Fig. 4). Sample 575 is from a coarse-grained band consisting of about 72 percent phenocrysts, ½–1 cm across. Sample 576 is

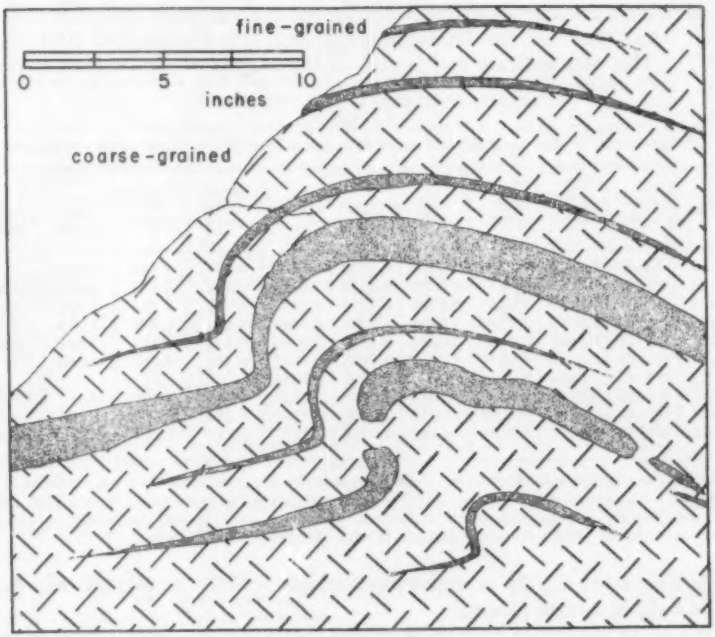

FIG. 4. Sketch of a banded unit in the Animas stock. The unit shows primary drag-folding.

from a fine-grained band 3 feet away, consisting of about 75 percent groundmass crystals, up to 1 mm across. Phenocrysts in both rocks are identical in composition and size, and groundmass minerals are, likewise, identical in composition and size. Sample 575 has almost 2½ times by weight more heavy residue and almost 6 times more zircon and apatite than sample 576. Yet zircon reduced major axes for the two samples are the same. It is noteworthy that in this case there has been no sorting of size or shape of the zircons.

These observations indicate that the banding is caused by differential movements of crystal mush and magma. This type of banding may be compared

with the concentration of blocks of ice in bands on slow-moving rivers, or the alignment of morainic material on glaciers. The results render it even more probable that zircon has crystallized in the intratelluric phase of the magma.

When the data of Table 2 are compared with those of the Bald Mountain batholith, Oregon (Table 3), it is evident that zircons of the Animas stock show a greater variation in mean length and width (maximum variation resp. 0.08 and 0.03 mm) than those of the Bald Mountain pluton (maximum variation resp. 0.02 and 0.01 mm). Comparisons show that in many samples from the Animas stock differences in mean length and width of zircons are significant at the chosen level of confidence ($p \leqslant 0.05$). Values for the coefficient of correlation are also somewhat lower for the Animas stock (range 0.53–0.72; mean 0.62) than for the Bald Mountain batholith (range 0.67–0.84; mean 0.74). This may indicate that zircons in the magma of the Animas intrusive

TABLE 3

PARAMETERS OF ZIRCON SAMPLES FROM THE BALD MOUNTAIN BATHOLITH, OREGON*

Index	$\bar{x}$ (mm)	$\bar{y}$ (mm)	s_x (mm)	s_y (mm)	a	r	Slopes compared z	Positions compared z	$\bar{x}$ compared	$\bar{y}$ compared
11	0.1059	0.0625	0.0388	0.0207	0.5332	0.7187	0.804	0.945	*2.638*	1.882
84	0.1109	0.0640	0.0414	0.0203	0.4954	0.6984	0.501	0.479	1.068	1.012
182	0.1242	0.0690	0.0434	0.0208	0.4793	0.7233	1.101	1.271	*2.811*	1.941
239	0.1202	0.0702	0.0382	0.0195	0.5098	0.8403	0.003	0.211	1.759	*2.711*
139	0.1128	0.0640	0.0406	0.0213	0.5230	0.6704	0.444	0.358	0.501	0.988
142	0.1129	0.0646	0.0433	0.0230	0.5188	0.7672	0.329	0.297	0.464	0.611
MGT_2	0.1145	0.0657	0.0411	0.0209	0.5097	0.7364				
116	0.1326	0.0528	0.0562	0.0285	0.5070	0.5529	0.081	*3.106*	*4.502*	*6.323*
148	0.1184	0.0535	0.0506	0.0234	0.6401	0.7768	*4.254*	*2.706*	1.037	*6.740*
465	0.1139	0.0451	0.0464	0.0165	0.3567	0.4937	*5.713*	*7.504*	0.168	*13.377*

* First four samples are tonalites. Next two samples are granodiorites from the core of the batholith. The mean growth trend (MGT_2) has been calculated from these six samples. Last three samples are younger intrusives in the batholith; 116 and 148 are granodiorites, 465 is a quartz monzonite. Each sample is compared with the mean growth trend.

crystallized more rapidly or under more variable (P, T) conditions than those in the Bald Mountain magma.

It may be concluded from these results that a granitic stock emplaced near the surface will in general have similar zircons throughout. However, the effects of sorting and magmatic corrosion may be sufficiently pronounced to result in significant differences in reduced major axes determined for zircon concentrates of a few of the samples, at the chosen level of confidence ($p \leqslant 0.05$).

ZIRCONS OF THE OAK CREEK TUFF AND THE WALNUT WELLS VENT

Zircons of 4 samples of Oak Creek quartz latite tuff have been measured. Locations of the samples are shown on Figure 2. The samples are within a one-mile radius from the Animas stock, are a maximum of 3½ miles apart, and have a maximum vertical separation of 775 feet.

Field- and laboratory data indicate that the Animas stock has served as source for the tuff, although the latter is slightly earlier than the intrusive rock of the stock. Evidence leading to this conclusion is; (1) the tuff thins when traced away from the stock in all directions, from a maximum of 1,500 feet or more near the intrusive, (2) planar structures in the tuff dip away from the stock, (3) linear flow streaks strike transversally to the stock and dip away from it, (4) phenocrysts in the tuff decrease in size and amount when traced away from the stock, (5) mineral compositions of both phenocrysts and groundmass minerals in the tuff and the stock are strikingly similar, (6) bulk chemical compositions of intrusive and extrusive rocks are alike (Table 4).

TABLE 4

CHEMICAL ANALYSES OF ROCKS FROM THE ANIMAS STOCK, THE OAK CREEK TUFF, AND THE WALNUT WELLS VENT, NEW MEXICO*

Index	6	707	A_{14}	A_3
SiO_2	66.08	63.47	64.73	61.15
TiO_2	0.59	0.69	0.60	0.77
Al_2O_3	12.23	16.95	17.40	18.19
Fe_2O_3	7.40	3.08	3.64	3.69
FeO	0.71	1.56	0.36	0.92
MnO	0.06	0.07	0.03	0.05
MgO	1.31	1.73	1.17	1.84
CaO	2.52	3.70	1.91	3.46
Na_2O	3.85	3.94	3.85	4.07
K_2O	3.95	3.65	4.14	3.45
P_2O_5	0.11	0.10	0.17	0.15
H_2O^+	0.62	0.75	1.61	1.46
H_2O^-	0.21	0.20	0.58	0.66
CO_2	0.34	0.16	0.00	0.00
Total	99.98	100.05	100.19	99.86
C.I.P.W.	1,423	1,423	1,423	1,424

* Analyst H. B. Wiik, Helsinki, Finland.

Index:

6,707. Quartz monzonite-porphyry, Animas stock.
A_{14}. Oak Creek quartz latite tuff.
A_3. Monzonite, Walnut Wells vent.

Zircons of two samples of monzonite from the Walnut Wells vent, 6 miles south of the Animas stock, have also been examined. The samples are ⅓ mile apart and differ 350 feet in elevation. The vent occupies a similar position in the stratigraphic volcanic sequence of the region as the Animas stock and the two bodies are therefore regarded to be penecontemporaneous. Although the vent rocks are slightly more mafic (Table 4), similarities in chemical and mineralogical compositions of rocks from vent and stock indicate that they may be consanguineous. Microscopic examination of the 6 zircon concentrates shows that they are similar to those of the stock with regard to variability of crystal forms and sizes, presence of a majority of highly faceted, football-shaped crystals and small proportions of elongated prismatic individuals of

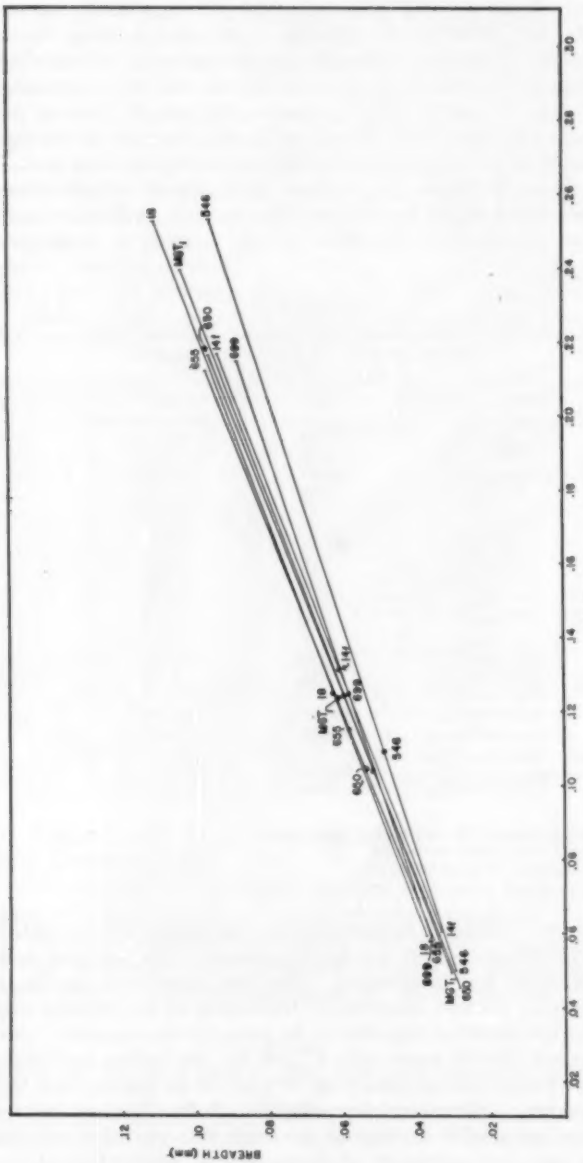

FIG. 5. Reduced major axes of zircon samples from the Oak Creek tuff and the Walnut Wells vent.

simple habit, degree and extent of rounding, and color variations. Honey brown, vermicular inclusions are also typical of the crystals of these six concentrates.

Reduced major axes of zircons of the 6 samples are compared in Figure 5 with the mean growth trend of zircons from the Animas stock. Statistical parameters and z values are listed in Table 5. Visual inspection of Figure 5 shows a pronounced similarity between all the reduced major axes. Statistical comparison indicates that all reduced major axes have the same slope and that only one tuff (sample 546) is significantly different in position of its reduced major axis. However, sample 546 shows distinct affinities with zircons of the Animas stock and is, for example, not different in slope or position from sample 6 (Table 2).

Sample 699 is a tuff collected within 15 feet from the contact with the Animas stock (Fig. 2). It has the same amount of heavy residue and zircon concentrate as tuffs collected farther away from the contact. Samples from

TABLE 5

PARAMETERS OF ZIRCON SAMPLES FROM THE OAK CREEK TUFF, THE WALNUT WELLS VENT, AND THE ANIMAS STOCK, NEW MEXICO*

Index	$\bar{x}$ (mm)	$\bar{y}$ (mm)	s_x (mm)	s_y (mm)	a	r	Slopes compared z	Positions compared z
148	0.1310	0.0606	0.0406	0.0160	0.3942	0.6140	0.513	0.825
18	0.1250	0.0630	0.0480	0.0188	0.3905	0.6521	0.401	0.769
546	0.1091	0.0491	0.0471	0.0156	0.3305	0.5485	1.678	*2.280*
699	0.1244	0.0588	0.0464	0.0160	0.3455	0.5260	1.121	1.221
650	0.1034	0.0514	0.0437	0.0179	0.4093	0.6567	1.014	1.027
655	0.1149	0.0582	0.0408	0.0167	0.4078	0.6039	0.938	1.189
MGT_1	0.1269	0.0605	0.0520	0.0196	0.3786	0.6189		

* First four samples are Oak Creek quartz latite tuff. Next two samples are monzonite from Walnut Wells vent. Each sample is compared with mean growth trend of the Animas stock (MGT_1).

the stock near contacts also do not show higher amounts of zircon concentrates than more centrally located rocks. There is therefore no evidence in the Animas stock of enrichment in zircon at contacts (c.f., Karakida, 3).

Results obtained indicate that the Animas quartz monzonite-porphyry, the Walnut Wells monzonite, and the Oak Creek quartz latite tuff stem from the same magma. They also lend further support to the idea that zircon crystallized in the intratelluric phase of the magma. Finally they demonstrate that even in volcanic rocks zircon studies may be used successfully to trace a particular flow or tuffaceous bed, and to correlate extrusive and intrusive derivatives of the same magma.

ZIRCONS OF DIFFERENT GRANITIC ROCKS

It is not sufficient to show that zircons of consanguineous granitic rocks have similar reduced major axes, but it must also be demonstrated that zircons of different granitic rocks have significantly different reduced major axes.

Taubeneck (7) has found that only the main phases of the Bald Mountain batholith have zircons with like reduced major axes, but three associated younger intrusives have zircon reduced major axes which differ from one another and also from those of the main batholithic phases (Table 3). Other comparisons are made in this paper.

In Figure 6 reduced major axes for zircons of 6 different granitic rocks of magmatic origin are compared. These include rocks from New Mexico, Oregon, and Idaho. Statistical parameters and z values are given in Table 6. Visual inspection of Figure 6 shows that the mean growth trend of zircons for the Bald Mountain batholith (Cretaceous) in Oregon, the zircon reduced major axis of a tonalite from the Kaniksu batholith (Cretaceous?) in Idaho, that of a Precambrian granite from the Little Hatchet Mountains, New Mexico, and that of a Cretaceous to Tertiary tonalite from Lordsburg, New Mexico,

TABLE 6

PARAMETERS OF ZIRCON SAMPLES FROM SIX DIFFERENT GRANITES*

Index	$\bar{x}$ (mm)	$\bar{y}$ (mm)	s_x (mm)	s_y (mm)	a	r	Slopes compared z	Positions compared z
1006	0.1014	0.0639	0.0280	0.0173	0.6189	0.7333	*6.599*	*7.920*
C–7	0.1458	0.0670	0.0499	0.0190	0.3804	0.7821	0.067	1.276
L–6	0.0748	0.0475	0.0180	0.0099	0.5525	0.4364	*4.249*	*8.224*
LL–11–1	0.1017	0.0338	0.0365	0.0122	0.3343	0.5572	1.543	*3.554*
MGT_2	0.1145	0.0657	0.0411	0.0209	0.5097	0.7364	*4.531*	*6.897*
MGT_1	0.1269	0.0605	0.0520	0.0196	0.3786	0.6189		

* Each sample is compared with the mean growth trend of the Animas stock.

Index:

1006. Granite, Little Hatchet Mountains, New Mexico.
C–7. Quartz monzonite-porphyry, Hanover, New Mexico.
L–6. Tonalite, Lordsburg, New Mexico.
LL–11–1. Tonalite, Kaniksu batholith, Idaho.
MGT_2. Mean growth trend, Bald Mountain batholith, Oregon.
MGT_1. Mean growth trend, Animas stock, New Mexico.

are distinctly different from the mean growth trend of zircons from the Animas stock. However, the Cretaceous to Tertiary quartz monzonite-porphyry from Hanover, New Mexico, has a zircon reduced major axis which resembles that of the Animas stock. Statistical comparisons confirm these impressions; slopes of four of the reduced major axes are distinctly different from that for the Animas zircons, but the Hanover zircons have a reduced major axis with similar slope and position as the mean growth trend of zircons from the Animas intrusive.

This similarity nicely shows the limitations of the method of the reduced major axis. It can be demonstrated by this method that two zircon samples are distinctly different, but two decidedly different samples may yet by chance have similar reduced major axes. In the present example there are distinct differences between the Hanover zircons and those from the Animas stock. The coefficient of correlation of the former is considerably higher than those

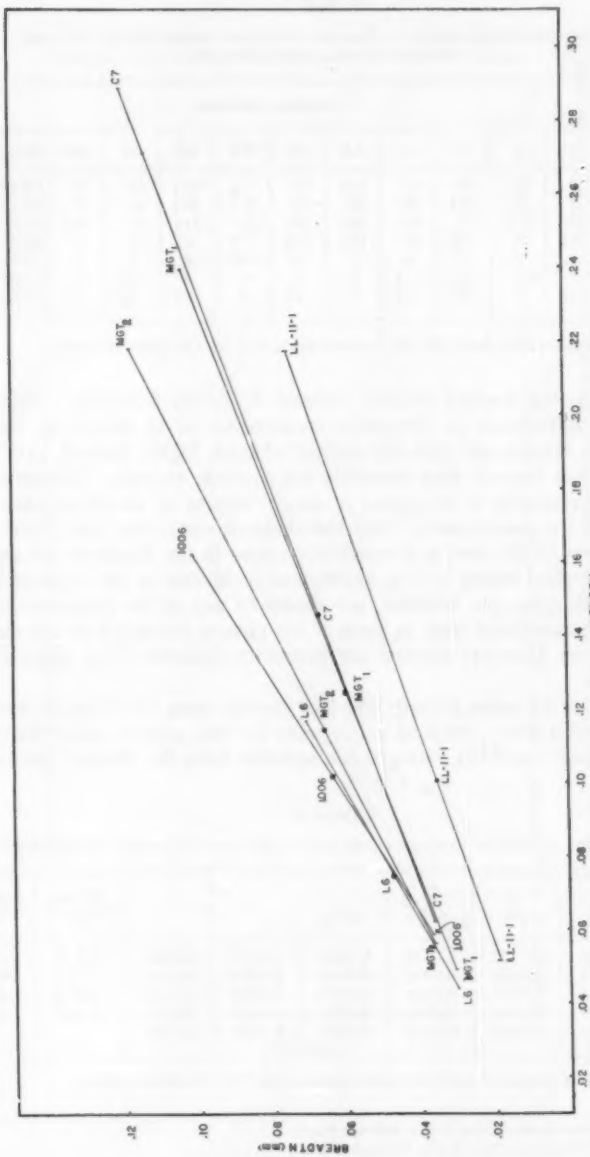

FIG. 6. Reduced major axes of zircon samples from six different granites.

TABLE 7

ELONGATION-FREQUENCIES OF ZIRCONS FROM THE ANIMAS STOCK AND THE HANOVER STOCK, NEW MEXICO*

1/b interval index	Frequency (percent)											
	1	3	4	6	548	575	576	591	707	844	Mean	C-7
1.00–1.49	20	17½	18	13	15½	11	11½	14½	10	15	14.60	5
1.50–1.99	33	38	38½	30	34	26	24½	34½	26	37	32.15	26
2.00–2.49	28	27½	27	39	33½	26	31	31½	36	32½	31.20	50
2.50–2.99	8½	8	5½	12	10½	15½	15½	9	14	8	10.65	15½
3.00–3.49	4	5	5	4	3	9	4½	4	5	4	4.75	2½
3.50–3.99	3	1	2½	½	2	5	5	4	4½	1	2.85	½
⩾4.00	3½	3	3½	1½	1½	7½	8	2½	4½	2½	3.80	½

* First ten samples and mean for the Animas stock, C-7 for the Hanover stock.

determined for the Animas zircons (column 7, Tables 2 and 6). There are also distinct differences in elongation-frequencies, as is shown in Table 7. The Hanover zircons are typically football-shaped, highly faceted, and colorless, and in this respect they resemble the Animas crystals. However, the characteristic minority of elongated prismatic zircons of simple crystal habit, present in all the concentrates from the Animas stock, the Oak Creek tuff, and the Walnut Wells vent, are completely absent in the Hanover concentrate. The equally typical honey brown, vermicular inclusions in the crystals of the first three rock types are, likewise, not shown by any of the Hanover zircons. It is therefore concluded that, in spite of the chance similarity of the reduced major axes, the Hanover zircons are distinctly different from those of the Animas stock.

In Figure 7 the mean growth trend of zircons from the Animas intrusive is compared with zircon reduced major axes for two granitic xenoliths in the stock (samples 9 and 556), one granitic xenolith from the Walnut Wells vent

TABLE 8

PARAMETERS OF ZIRCON SAMPLES FROM XENOLITHS AND A YOUNGER EXTRUSIVE*

Index	$\bar{x}$ (mm)	$\bar{y}$ (mm)	s_x (mm)	s_y (mm)	a	r	Slopes compared s	Positions compared s
9	0.0813	0.0490	0.0322	0.0356	1.1041	0.8501	*15.737*	*23.277*
556	0.0854	0.0558	0.0285	0.0186	0.6529	0.7862	*7.748*	*9.047*
608	0.1021	0.0630	0.0306	0.0153	0.5002	0.6956	*3.670*	*4.975*
739	0.0672	0.0409	0.0162	0.0098	0.6085	0.6342	*5.849*	*6.356*
MGT_1	0.1269	0.0605	0.0520	0.0196	0.3786	0.6189		

* Each sample is compared with the mean growth trend of the Animas stock.

Index:

9,556. Granitic xenoliths in the Animas stock.
608. Granitic xenolith in the Walnut Wells vent.
739. White rhyolite tuff.
MGT_1. Mean growth trend, Animas stock.

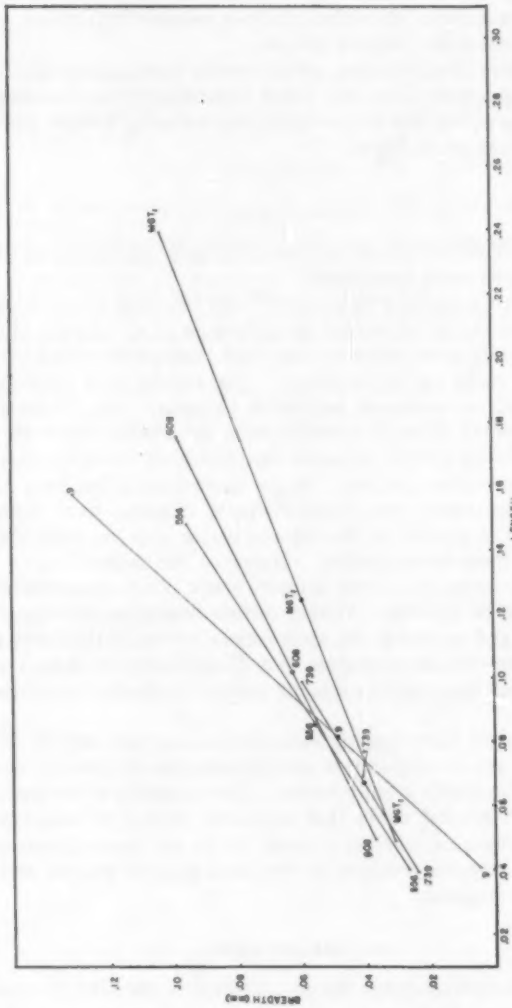

FIG. 7. Reduced major axes of zircon samples from granitic xenoliths in the Animas stock and the Walnut Wells vent, and from the younger White rhyolite tuff.

(sample 608), and one sample from the younger White rhyolite tuff (sample 739) which also outcrops in the Walnut Wells quadrangle. Statistical parameters and s values are listed in Table 8. Both visual inspection of Figure 8 and statistical comparisons show that all these reduced major axes are widely different from that of the Animas zircons.

Thus it has been demonstrated, within certain definite limitations, not only that reduced major axes of zircons which crystallized from the same granitic magma are the same, but also that reduced major axes of zircons which formed in different magmas are different.

CONCLUSIONS

This paper is a report on one of a series of pilot studies in which the role of zircon in granitic rocks is explored.

Granitic plutons have been carefully selected for these zircon studies. The granitic rocks chosen are of normal and common type. Zircon studies have been carried out only after sufficient field- and laboratory evidence concerning the origin of the rocks had accumulated. The results have confirmed earlier impressions based on work of qualitative character (c.f., Poldervaart, 6), namely that zircon is of early crystallization in granitic rocks of magmatic origin and that zircons exhibit the same morphological characteristics throughout each of the intrusives studied. At the same time it has been established that granitic rocks which stem from different magmas have distinctly different zircons. The method of the reduced major axis has been shown to be of much value in these zircon studies. However, the reduced major axis does not completely describe the zircon sample, hence other characteristics of the sample should not be ignored. Within certain limitations resulting from the effects of sorting and corrosion, the same conclusions as to similarity of zircons in derivatives from the same magma and dissimilarity of zircons in derivatives from different magmas can also be applied to shallow intrusives and to extrusives.

These conclusions have considerable significance, not only in the field of petrogenesis, but also in exploration and exploitation of minerals of economic importance associated with granitic rocks. Zircon studies of the type described here can establish beyond doubt that a granitic rock is of magmatic origin. They can also determine whether granitic rocks are consanguineous or not, and differentiate between products of the same granitic magma and those of older or younger magmas.

ACKNOWLEDGMENTS

Alper wishes to acknowledge the co-operation of the New Mexico Bureau of Mines and Mineral Resources, under whose auspices the study of the Walnut Wells quadrangle has been carried out. Tenure of a Columbia University Fellowship, and a grant from the Kemp Memorial Fund, also aided the project.

The zircon work has been made possible through a grant from the Eugene Higgins Fund of Columbia University.

CORNING GLASS WORKS,
CORNING, N. Y.,
AND
DEPARTMENT OF GEOLOGY,
COLUMBIA UNIVERSITY,
NEW YORK 27, N. Y.,
May 1, 1957

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Economic Geology
Vol. 52, 1957, pp. 972–974

SCIENTIFIC COMMUNICATIONS

COMPARISON OF SOME WOLFRAMITE DEPOSITS IN EGYPT AND FRANCE

S. TOSSON

The author studied some wolfram tungsten deposits in the South Eastern Desert of Egypt (Zarquet Na'am) and in the southwestern part of France (La Châtaigneraie-Cantal). This paper represents a condensed resume with conclusions of the work written in French,[1] which revealed that ore formation was the result of concentration of appropriate elements during the processes of metamorphism and granitization that affected these areas.

The original study covers some 300 pages of petrographical, geochemical, structural and mineralogical details with pertinent illustrations. The author started his studies in 1952 in the Zarquet Na'am area, south of the Egyptian Eastern Desert; Lat. 23°46′40″N and approximate Long. 34°40′E, at a distance of about 90 km from the Red Sea coast and 174 km from the Nile. From a petrographical viewpoint, this area can be divided into:

1. The hill of Hemeirat Abu Haad, which contains mineralized quartz veins with wolframite in granite and greisen.
2. A variety of rocks (acidic volcanic, microgranite, grawacke, etc.) forming mineralized low hills, nearby and partly covering the base of the above hill.
3. A series of greenish-white volcanic rocks situated northwest of the above low hills.
4. The mountain of Zarquet Na'am (highest peak in the area) featuring mainly alkaline granite and quartzitic syenite in contact with amphibolite.
5. Granitic and dioritic rocks surrounding the area of Zarquet Na'am.
6. Different dikes.

The second area (La Châtaigneraie-Cantal), south-west of France, contains three mines containing wolframite in mica schist:

a) Leucamp in contact with a non-mineralized granitic mass.
b) Teissières Les Boulies about 2 km north of Leucamp.
c) Murol at about 3 km east of Leucamp.

[1] Tosson, Salama (1957), Études Géologiques et métallogèniques de quelques régions de Mines de Wolfram en Egypte et en France. Ecole Supérieure de Géologie Appliquée et Prospection Minière—Nancy, France.

COMPARISON BETWEEN THE TWO AREAS

The apparent differences between the two areas are less marked with respect to the origin of mineralization.

Distinctive Characteristics.—1. The ages of the deposits are not the same; mineralization of La Châtaigneraie is anti-Stephanien—undoubtedly Hercynien—and that of Zarquet Na'am is Precambrien.

2. Difference in country rocks: at Zarquet Na'am they are granites and microgranites, but at La Châtaigneraie they are mica schists of sedimentary origin.

3. The minerals associated with the wolframite in Zarquet Na'am are cassiterite and fluorite, as against pyrite and tourmaline in La Châtaigneraie.

4. The wolframite mineralization in Zarquet Na'am in places is in direct contact with the country rocks, and in other places disseminated in the granite; these phenomena were not observed in La Châtaigneraie where the country rocks are of mica schist. The mineralized quartz veins do not extend through the granite mass bordering the Leucamp mine.

Similarities.—1. Mineralization in both cases, borders the granite masses, but never extends through them.

2. The veins, in both areas, are of different width and length, but their form on the whole is identical, i.e., somewhat lenticular.

3. In Zarquet Na'am as well as in La Châtaigneraie, there had been liberation of K and Li during metamorphism. These elements enter into the constitution of minerals of later formation, such as muscovite and zinnwaldite, which surround the mineralized veins.

4. Trace elements, in relatively high proportion, were detected spectroscopically in the country rocks. These elements could be concentrated if certain combined conditions prevailed.

5. In the two areas, the granitization and metamorphism reached an advanced stage. It would rather seem as though the mineral deposit formation had some relation with these processes. The role of granite in the formation of these veins is indirect, inasmuch as the trace elements of the deposits in granite are lower than these in the mother rocks, which seems to be in confiict with the classic theories that these elements are part of the granite itself.

In conclusion, it can be stated that the concentration of the wolframite is the result of metamorphism and granitization processes.

Metamorphic transformations are likely to release large quantities of elements, in a dispersed state, which under favorable conditions, could be localized and concentrated in the form of mineral veins.

In the regions of Zarquet Na'am and La Châtaigneraie, wolfram (oxyphile) owing to its non-petrogenic nature, migrated during metamorphism towards the border of the granite mass and not deeply inwardly; a noticeable phenomenon in several other similar mines.

Indications are that the source of mineralization does not emanate from the granite itself, but the process of the formation of granite aids the concentration of the elements of the mineral deposits from their mother rocks.

Classification of ore deposits, based on the nature of their mother rocks, would be more perferable than that based on the theories of magmatic differentiation.

ACKNOWLEDGMENT

Thanks are extended to Prof. M. Roubault, Director of "Ecole Supérièure de Géologie de Nancy—France," for the assistance accorded to the author, which enabled him to produce the original work.

FACULTY OF SCIENCE,
ALEXANDRIA UNIVERSITY, EGYPT,
Oct. 14, 1957

Economic Geology
Vol. 52, 1957, pp. 975-976

DISCUSSIONS

SHEARING AND URANIUM MINERALIZATION, NORTHERN TERRITORY, AUSTRALIA

Sir: In the May issue of ECONOMIC GEOLOGY another paper by J. Rade about mineralization in the Northern Territory of Australia appeared. Much of the criticism that was levelled by Walpole (ECONOMIC GEOLOGY, vol. 52, no. 6) at a previous rather similar article by Mr. Rade can also be directed at this paper, but we feel that some additional comment is necessary because the author has expounded his ideas in such a way as to make it impossible for readers to distinguish between information that geologists would see on the ground and that which Mr. Rade has deduced to fit in with the postulated effects of this bathyrheal underflow with which he is so obsessed.

The author could hardly have chosen three more unimpressive and insignificant uranium occurrences on which to build a general theory of uranium mineralization.

Confident statements such as "It should be noted that similar weak movements along north-east trending cross-fractures are characteristic of the whole of the northern part of the Northern Territory" are regarded as subjective and misleading by those of us who have a more detailed knowledge of this part of the Northern Territory. Many of his statements are correct, but others are directly counter to the results of our detailed mapping, and no attempt is made to justify them by observed facts or interpretative discussion.

Perhaps the most enlightening criticism we can make concerns the George Creek Prospect which is quoted as an example of a sheared anticline. In support of this contention the author provides a geological map of an area of about 600 feet by 300 feet at the George Creek Prospect on which westerly dipping bedding and some thirty fractures are shown. Mr. Rade states that the prospect is "situated on the side of an anticline trending approximately north-south which has been sheared along its length, the east side moving north and the west side south."

On this basis, he interprets small north-west trending shears, with which uranium is associated, as tension fractures. In fact, the fracture pattern of the prospect could just as well be interpreted as a set of shear joints, with some tension joints, consequent on the compression that produced the folding.

The essential point in Mr. Rade's story is the existence of a sheared anticline, but neither the axis of the anticline nor the shear is shown on his map and the generous reader must assume that both lie beyond the eastern margin of the plan.

Geological mapping by the Bureau over a wider area than that covered

by Mr. Rade has in fact located the anticlinal axis 300 feet east of the prospect but there is no sign of the shear we are led to believe exists.

Mr. Rade is entitled to his interpretation of small fractures at the prospect but we must object to his misleading readers by recording as fact an unmapped and invisible shear and of using this type of "evidence" to clutter up the geological record with unscientific flights of fancy involving "geoplasma" and "bathyrheal underflow."

N. H. Fisher and L. C. Noakes

Bureau of Mineral Resources,
Canberra, Australia,
Oct. 16, 1957

POSSIBLE GENESIS FOR ANTHRAXOLITE

Sir: Among comments that I have received on my paper Is Anthraxolite Related Genetically to Coal or to Oil? (Econ. Geol., v. 51, no. 7, p. 649–664) was a most interesting suggestion concerning another possible origin for anthraxolite that was sent to me by Martial P. Corriveau, Preparation Engineer, Clinchfield Coal Company, Dante, Virginia. Mr. Corriveau's comment was as follows: "In low temperature carbonization testing of coal it was noted that fluidity of the coal occurs at around 400° F. The low ash component—bright coal, vitrain—becomes fluid before the other components, and flows like lava. (Actually, this component may be only one so acting.) Once the volatile matter of the coal is driven off, the char becomes brittle. The resulting char has an oily to sub-metallic lustre. These tests were run at nearly atmospheric pressure, hence it can be presumed that increasing pressure will reduce the temperature at which the coal becomes fluid."

It appears to me that this is a most interesting possibility and one that should be considered not only for anthraxolite but also for some of the other natural hydrocarbons such as impsonite.

R. V. Dietrich

Blacksburg, Virginia,
August 12, 1957

Economic Geology
Vol. 52, 1957, pp. 977–988

REVIEWS

Boundary Control and Legal Principles. By CURTIS M. BROWN. Pp. 275; figs. 93. John Wiley and Sons, Inc., New York, N. Y. 1957. $7.50.

In this book the author, a civil engineer, "discusses and outlines legal principles that control the boundary location of real property."

The ten chapters contain condensed information on the legal elements and terms that determine what and where boundaries are. The book begins with an excellent outline of the surveying systems used in this country to describe property, continues with information on locating metes and bounds, locating subdivisions and conveyances lacking senior rights, locating reversion rights, and ends with two interesting chapters on "Writing Deeds" (a glossary of deed terms is also included) and "The Surveyor and His Duties." This latter chapter cites informative law suits in which surveyors have been held liable for damages because of the lack of "due care" in surveys. The author has suggested, therefore, that "to avoid liability the surveyor should err on the side of safety." Chapter eight, "Federal Mining Laws," is of greatest interest to the geologist but the general information contained on the less than ten pages of this chapter should add little to the knowledge that even tyro geologists have on this subject.

M. L. JENSEN

L'Évolution de la Lithosphère, I. Pétrogénèse, II. Orogénèse. By H. AND G. TERMIER. In two parts, pp. 940; figs. 152; maps 86. Masson, Paris, 1956. Price, bound, each volume 9,800 francs.

Henri and Geneviève Termier, two French scientists, have undertaken the publication of a new textbook of geology. This original book cannot fail to receive the utmost welcome by all those who are interested in earth sciences.

A first volume was issued in 1952 entitled: "Histoire géologique de la Biosphère," which was reviewed by me.[1]

Since then two other parts have been issued under the same title: "L'évolution de la Lithosphere," the first part dealing with Petrogenesis, the second part with Orogenesis in two important volumes.

These two parts are so united that I have thought it advisable to review them together inasmuch as their publication appeared only a short time apart.

I. PETROGENESIS

The scheme of this work is rather different from that of classical text-books.

The first part of the book is devoted to generalities, namely to present day opinions about the constitution of matter, and the restatement of the classical table of Mendeljeff. Following this the authors retrace the ideas that arose successively regarding the origin of the earth from the formerly classical theory of Laplace. They dispute the genesis of the hydrosphere in relation to the appearance of life; then follows energy and its alterations; particular importance is given to lack of isostasy, leading the authors to enter the domain of orogenesis.

Taking up the structure of the atom, concisely recalled, leads the authors pro-

[1] ECON. GEOL., v. 49, p. 103, 1954.

gressively towards the idea of migration of material in the lithosphere, and also to the knowledge of mineral inclusion in rocks, and to geochemistry. Taking account of these ideas, they deal with radioactivity and the dating of rocks.

The outstanding problems of petrogenesis are explained in the main part of the book. It starts with considerations of the geological evolution of the lithosphere, the weak areas of the earth's crust, which originate geosynclinal zones and prelude orogenic genesis. Then follows the description of the "drama-type." In fact, this is already an incursion in the domain of orogenesis.

Coming back to their subject, the authors deal with the classification of eruptive rocks, magmas, volatile elements, and their cycle in the lithosphere ("domaine de l'instable"). In a broader outlook, they deal with sima and volcanites, sial and plutonites. The consideration of the latters bring the authors to examine the influence of dynamic actions in petrogenesis, namely mylonites and schistosity, then metamorphism and metasomatism with its equilibrium and de-equilibrium, characterized by material exchanges. Thereupon, they emphasize that metasomatism is one of the main causes for the evolution of the lithosphere. The chapter devoted to these problems ends with considerations on the role and the future of sediments and basic rocks.

Another chapter is devoted to the complexity of the problems of the origin of granite, and of the role played by granite and granitisation in the structure of the earth's crust. Still another chapter deals with sialic volcanism in orogenic areas.

Finally the work ends with ideas regarding converging and diverging rocks.

This book brings to the informed readers a concise aspect of well-known ideas regarding the genesis and the evolution of rocks in connection with the structure of matter; in connection also with the outstanding laws that have presided in the formation of the present earth's crust. Of course, several discussions might arise, as I personally did in regard to schistosity,[2] and discussions of the origin of granite may also arise. Weakness in the argumentation as well as in the distribution of chapters may cause some criticism, as might arise in any work of this kind. However, the authors deserve congratulations for the tremendous effort they have undertaken in the accomplishment of their work. I should add that the volumes are abundantly and plainly illustrated by examples taken in various parts of the world.

II. THE OROGENESIS

This part of Henri and Geneviève Termier textbook of geology appearing into two volumes "is essentially devoted to the history of numerous orogenes whose progressive unit has contributed to the erection of the present physiognomy of the earth."

First, the authors retrace some generalities. They mark the link between earthquakes and recent deformations easily measured on one hand, and orogenesis whose growth is extremely slow, on the other.

Classical ideas regarding seisms and their distribution are first traced. Their probable causes and their application to the knowledge of deep zones and geophysics are pointed out, as well as their interest concerning the control of theories on orogenesis. The introduction to structural analysis starts with a series of definitions. Then follows the study of the basement tectonics and of the behaviour of rocks in regard to determined depth, from superficial slopes of big thrusts, from tectonics produced during sedimentation, to infrastructure tectonics. Special importance is given by the authors to vertical and tangential movements taking partial account of the present ideas on the subject.

[2] C. R. Acad. Sc. Institut de France, février 1956.

The second part of the book deals with oceans. It may be regretted that the authors have devoted such a restricted space to this problem considering that two-thirds of the earth-surface is covered by water. One also regrets that the authors did not mention the problem of eventual permanence of large oceans and have only ascertained the existence of two sinking oceans and two seismic oceans—thus comparing characters that apparently do not correspond.

The two following parts deal with Laurasian continents on one hand and Gondwanian on the other. Abundant data are given, though in part dissimilar. One wishes that a more complete synopsis had been reported. Doubtless, the authors have counclusions about Gondwanian areas, but one might expect to find a critical review of the actual opinions regarding problems of large earth-surface interest.

In a fifth part, tethysian orogenes are examined concerning the outstanding features of orogenesis in Europe, North Africa, Asia, Central America, in addition to zones already mentioned under the name of Laurasian and Gondwanian continents. In the same leading principle, one may find the review of knowledge relating to main orogenies that have risen in place of the "Tethys," which represents such a remarkable feature in the earth's crust evolution. Once more, it is not possible to draw up a detailed analysis of this part of the work. Anyway, the reader will find a lot of information that will be of great help for his further researches. One might also regret that there are not more recent references in the bibliography—namely on areas that I know from personal experience. In this description of part of the old world, which has for such a long time been studied by geologists, it might have been useful to find a short review of probable connections between orogenes now separated by the sea or by large discordant horizontal formations. Also, one may say that in the case of some orogenes, the authors give too great importance to the relation of magmatic rocks with other rocks. These are natural deficiencies in such an estimable work, bringing to its readers rich data illustrated by abundant references to all parts of the world.

However, the review of known facts about the earth's crust evolution should lead to an opinion regarding the laws controlling earth history during geological times. Like myself, one will regret that the authors did not find it advisable to devote to the last part of their work, the review of these laws. Surely, they give their readers an essay of megatectonics supplying information on problems interesting in the evolution of the superficial earth crust: nuclei, permanent zones and zones of weakness, reversion of relief, mentioned by the law of Haug, though disputable;[3] geosynclinal migrations about which France, Belgium, England as well as Australia may be listed; the classification of orogenes and their mutual connections. This part ends with some very summarized ideas on the evolution of the lithosphere and the consequential effects of megatectonics on palaeogeography, and on the history of the Biosphere.

I will not end with a regret. In reviewing the work of the Orogenesis of the authors, I have mentioned my criticisms, which may not be shared by many of my colleagues. But I do say that their work is a most valuable one because it brings to French geologists, independently of original ideas, an abundant documentation with profuse references. It realizes an outstanding contribution to geological sciences. As I said before about "Petrogenesis," the authors deserve grateful thanks for the enormous amount of work they have done.

P. FOURMARIER

LIEGE, BELGIUM,
Sept. 27, 1957

[3] P. Fourmarier, La règle de la compensation approchée des volumes. Ann. Soc. Géol. Belgique, Bull. Liége, 1948–1949.

Occurrence of Oil and Gas in West Texas. Edited by FRANK A. HERALD. Pp. 456. Univ. of Texas Pub. No. 5716, Bureau of Economic Geology, Austin, Texas, 1957. Price, $10.00.

This volume results from a cooperative effort between the West Texas Geological Society and the Bureau of Economic Geology. This is the second volume of the series entitled "Occurrence of Oil and Gas in Texas" being issued by the University of Texas.

The volume is made up of articles by 104 geologists and gives a complete summary of conditions in 112 oil fields. For each field there are given the location, history, occurrence of oil and gas in reservoir rocks, stratigraphy, lithology, nature of traps, character of oil and gas, and production history. Structure maps, graphic rock sections, cross sections and logs are included for most fields. Folded colored maps accompany many of the field descriptions.

The book is an excellent reference on West Texas oil fields and includes much fundamental information on the occurrence of oil and gas generally. It also gives examples of research in oil and gas exploration. It is a book that will be desired by all Texas geologists and should be a part of all geological libraries.

A Treatise on Limnology—Vol. I, Geography, Physics, and Chemistry. By G. EVELYN HUTCHINSON. Pp. 1015; figs. 228. John Wiley & Sons, New York, 1957. Price, $19.50.

Most geologists in reading this title would think it probably does not contain much of interest for them. They are mistaken. This volume is by one of America's outstanding scientists, whose breadth of knowledge is great. Many will recall the author as the interesting writer of the "Marginalia" columns that have long been running in the *American Scientist*. In this bulky volume he covers the sequence of geological, physical, chemical, and geological events operating together in a lake basin.

The author states that his aim is to give as complete an account as is possible of the events characteristically occurring in lakes, and in this first volume to cover geographical and physico-chemical limnology.

The first chapter, "The Origin of Lake Basins," is a historical introduction of 163 pages, which is largely geological and descriptive of the various kinds of lake basins found throughout the world and of the various ideas advanced for their origin. It concludes with a 7-page classification of lakes, with examples of each, such as tectonic lakes, volcanic, glacial, landslide, solution lakes, etc. Following this are chapters on the morphometry and morphology of lakes; properties of water; the hydrologic cycle; hydromechanics; optical and thermal properties; the inorganic ions of rain, lakes, and rivers; oxygen in lake waters. Then follow chapters on the cycles or iron, phosphorus, sulfur, silica, minor elements, nitrogen, and organic matter, in lake waters. The volume is concluded with five extensive indexes, namely: symbols, bibliography and index of authors, index of lakes, index of organisms, and a general index.

After each of the chapter discussions are factual summaries that cover the particular discussion, and together provide a simple account of what is known about lakes.

The content of the volume is almost overwhelming. Each chapter is so complete that it constitutes the last word on the subject. The volume is bound to prove to be the outstanding reference on the geology, geochemistry, biology, and chemistry of lakes. For geologists and geochemists it will outdo what for many years was

accomplished by Clarke's *Data of Geochemistry*. It is a volume that will have to be a part of all geological, geochemical, biological, and chemical libraries.

Dr. Hutchinson has been on the faculty of Yale University since 1928 and is now Sterling Professor and Director of Graduate Studies in Zoology. His pursuit of knowledge of lakes has led him to most parts of the world where lakes occur.

The Porphyry Coppers in 1956. By A. B. PARSONS. Pp. 270. Amer. Inst. Min. Met. and Petrol. Engrs., New York, 1957. Price, $5.00 and 50 cts. foreign postage.

When *The Porphyry Coppers* appeared in 1933 it commanded the widespread interest of all people interested in copper, its mines, its metallurgy, and its financing. This new volume brings up to date the changes that have occurred in the 12 original porphyry coppers in the last 24 years. In addition, the history and developments of the 9 new porphyry coppers are included. These are the "new" Morenci, Yerington, Bagdad, Consolidated Copper Mines, Silver Bell, Lavender Pit, Castle Dome, Copper Cities, and San Manuel.

Whereas the first volume contained extensive discussions of technology and engineering, this volume contains less of the detailed technology and more discussions intelligible to the lay reader.

In the first chapter the author reviews "Twenty-five Years of Progress." He points out that the original 12 porphyries had produced up to 1931 some 17.4 billion pounds of copper worth 2.82 billion dollars. In contrast, up to the end of 1955 the output has been increased to 60.5 billion pounds worth 10.44 billion dollars. Some 50 percent of the world's production of copper is considered to come from the porphyry coppers. In this chapter there is also given the production of copper from 18 porphyry coppers for each year from 1905 to 1955. There is also defined "what is a porphyry copper?" Technologic progress is outlined and a discussion of "Cooperation between Government and Industry" is included.

The remaining chapters one by one deal with each of the porphyry coppers. The older ones are brought up to date in their mining, beneficiation, metallurgy, and financial matters. More data, including historical, is given for the newer deposits.

This volume should find wide interest among mining and metallurgical engineers interested in copper, as well as among economists, financiers, investment houses and investors.

Economic Geography of Ohio, 2nd Edit. By ALFRED J. WRIGHT. Pp. 245; figs. 122; tbls. 49. Ohio Department of Natural Resources, Division of Geological Survey, Columbus 10. Price, $2.00.

This volume is a revision of the author's geography of 1953 with much new text, many photographs, and up-to-date tables. The chapters include the history and geologic background and geomorphology for the present background of Ohio. Succeeding chapters take up agriculture, mineral industries, manufacturing, commerce. Five additional chapters deal with southwestern, northeastern, southeastern, northwestern and central Ohio. These five chapters consider the industries, agriculture, mineral resources, manufacturing, power and cities.

The volume should be of great interest to residents of Ohio and those interested in its geography.

BOOKS RECEIVED

JAMES M. ALLEN AND JOHN W. SALISBURY

Fenestella from the Permian of West Texas. M. K. ELIAS and G. E. CONDRA. Pp. 158; pls. 23; figs. 17; tbls. 10. Geological Society of America, Memoir 70, New York, 1957. *The 38 species and varieties, 27 new ones of Fenestella, described are mainly from the Permian of the Glass Mountains, West Texas. Four are from the lower Permian of the western Urals in Russia. Identified associated Bryozoa are also listed. Exhaustive study.*

Basic Research—A National Resource. Pp. 63; charts 3; tbls. 8. Price, 45 cts. National Science Foundation, Washington, D. C., 1957. *A report in nontechnical language of "the meaning of basic research in science, and how important it is to the Nation's economy, health and defense."*

The Structural Evolution of the Hunter-Manning-Myall Province New South Wales. G. D. OSBORNE. Pp. 79; pls. 3; figs. 10. Price, 15 sh. Royal Society of New South Wales, Monograph 1, Sydney, 1950. *Deformation of late Paleozoic age affecting Devonian to Permian rocks.*

Selected Studies of Colorado Pegmatites and Sillimanite Deposits. E. W. HEINRICH and J. E. BEVER. Pp. 55; figs. 21; tbls. 2. Price, $1.50. Quarterly of the Colorado School of Mines, Vol. 52, No. 4, Golden, 1957. *Three papers: Pegmatite Provinces of Colorado; Radioactive Mineral Occurrences; Occurrences of Sillimanite-Group Minerals in Park and Fremont Counties.*

Geology of Umm Salatît—El-Hisinât District. M. SABER MANSOUR, F. A. BASSYUNI and D. M. AL-FAR. Pp. 43; pls. 18. Price, P.T. 120. Geological Survey of Egypt, Cairo, 1957. *Areal geology of metamorphic igneous terrain of Precambrian age in central Egypt. Record of ancient gold workings. Chromite, asbestos, vermiculite and talc associated with ultrabasic rocks.*

Annual Report of the Fiji Geological Survey for the Year 1956. Pp. 9; fig. 1. Price, 1s 6d. Suva, 1956. *Summary of work done in 1956, bibliography and list of available maps. Manganese is most important economic product.*

Compte-Rendu Sommaire des Séances de la Société Géologique de France—1956. Paris. *Proceedings of French Geological Society for 1956. Selected papers and abstracts. In French.*

Publications on the Geology and Mineral Resources of Georgia. GARLAND PEYTON. Pp. 11; pl. 1. Georgia Geological Survey Circular 1 (5th ed.), Atlanta, 1957. *Map showing map coverage of Georgia, scale 1:1,000,000. Includes price list.*

Summary of Progress of the Geological Survey of Great Britain and the Museum of Practical Geology for the Year 1956. Pp. 84; tbls. 6. Department of Scientific and Industrial Research, London, 1957.

Reconnaissance Geology of the Leesburg Quadrangle, Lemhi County, Idaho. P. N. SHOCKLEY. Pp. 41; pls. 2; figs. 13; tbls. 2. Idaho Bureau of Mines and Geology, Pamphlet 113, Moscow, 1957. *Areal geology of terrain underlain largely by the upper Precambrian Belt series, smaller amounts of Ordovician and Tertiary sediments all overlain by Pleistocene drift. Economic products are cobalt, copper, radioactive rare-earth minerals, gold, tungsten, lead and silver.*

Australian National Committee on Geodesy and Geophysics. Report of the Sub-Committee on Vulcanology, 1953. Review of Volcanic Activity in the Territory of Papua-New Guinea, the Solomon and New Hebrides Islands,

1951–53. G. A. TAYLOR. Pp. 12; figs. 8. Naples, Italy, 1956. *Description of recent vulcanism in the South Seas.*

Geology of the Winnipeg River Area (Shatford Lake-Ryerson Lake) Lac du Bonnet Mining Division, Manitoba. J. F. DAVIES. Pp. 27; figs. 2; geologic maps 2. Manitoba Department of Mines and Natural Resources, Publication 56-1, Winnipeg, 1957. *Physical and economic geology of Precambrian terrain in eastern Manitoba. Beryl and lithium in pegmatite deposits. Area includes the Huron claim noted for uraninite in excess of 2,500 million years old.*

Étude Géotechnique de la Région de Casablanca. J. DELARUE, J. DESTOMBES, and A. JEANNETTE. Pp. 178; pls. 2; figs. 44; tbls. 23. Ministère de la Production Industrielle et des Mines Service Géologique, Notes et Mémoires No. 130, Rabat, Morocco, 1956. *Includes two short articles on soils and the mineral industry. Geologic map, scale 1:50,000.*

Upper Cretaceous Ostracoda from North Carolina. P. M. BROWN. Pp. 28; pls. 7; fig. 1. North Carolina Department of Conservation and Development, Bull. 70, Raleigh, 1957. *Description of 56 species, 27 of them new, of ostracods from the Upper Cretaceous of North Carolina.*

Report on the Recent Investigation of the Sumbu-Nkombedzi Coalfield, Chikwawa District. F. HABGOOD. Pp. 29, pl. 1; figs. 2; tbls. 12. Geological Survey of Nyasaland, Rept. No. 1, Zomba, 1956. *Rapid lateral and vertical variation in coal quality, high ash content of coal, and more complicated structure than previously believed make field unattractive commercially. Geologic map, scale 1:50,000.*

Annual Report for the Year 1956. Pp. 10. Price, 1 sh. Department of Water Development and Irrigation, Lusaka, Northern Rhodesia, 1957.

A Geologic Map of the Bend Quadrangle, Oregon and a Reconnaissance Geologic Map of the Central Portion of the High Cascade Mountains. HOWEL WILLIAMS. State of Oregon Department of Geology and Mineral Industries, 1957. *Geologic maps (2). Descriptive notes.*

Boletin de la Universidad Nacional de Ingenieria, Tomo XXX, Serie IV. J. DE LAS CASAS PASQUEL, C. A. URRUTIA, and L. O. DE ZEVALLOS. Pp. 72; figs. 11. Universidad Nacional de Ingenieria, Lima, Peru, 1957.

O Miocénico Marinho de Lisboa. J. C. BERKELEY-COTTER. Pp. 168. Communicações dos Serviços Geológicos de Portugal, Lisbon, 1956. *Faunal study of Miocene Marine deposits in the Lisbon area. In Portuguese.*

Publicaciones del Departamento de Cristalografia y Mineralogia, Vol. II, No. 3. Pp. 80; pls. 5; figs. 12; tbls. 11. Consejo Superior de Investigaciones Cientificas, Barcelona, 1956. *Papers dealing with x-ray crystallography, genesis of bauxite and the mineralogy of zircon-bearing sands. In Spanish; short summaries in English.*

The Geology of the Country Between Belingwe and West Nicholson. B. G. WORST. Pp. 215; pls. 25; figs. 4. Southern Rhodesia Geological Survey Bulletin 43, Salisbury, 1956. *Areal geology of a Precambrian terrain in southern Southern Rhodesia. Serpentine asbestos and gold ore the principal economic products. Occurrences of chromite, copper, corundum, iron ore, lead, limestone, magnetite, mica and tungsten are described. Geologic map 1:100,000.*

Revista de Minas e Hidrocarburos. Pp. 84; pls. 3; figs. 13; tbls. 9. Ministerio de Minas e Hidrocarburos, Republica de Venezuela, Caracas, 1957. *Mineral production statistics for the year 1956. 11,000,000 tons of iron ore produced.*

Alabama Geological Survey—University, 1952–57.

Museum Paper 34. New Genera of Anophthalmid Beetles from Cumberland Caves (Carabidae, Trechini). J. M. VALENTINE. Pp. 41; pls. 5.

Museum Paper 35. New Genera and Species of Cavernicolous Diplopods from Alabama. R. L. HOFFMAN. Pp. 13; pls. 2.

Bull. 66. Geology and Ground Water in the Monroeville Area, Alabama. J. B. IVEY. Pp. 116; pls. 12; figs. 33; tbls. 2.

Spec. Rept. 23. Geology and Ground Water of the Piedmont Area of Alabama. JACK BAKER. Pp. 99; pls. 2; figs. 13; tbls. 5.

Annual Reports for the Fiscal Year October 1, 1954–September 30, 1955. W. B. JONES. Pp. 37; figs. 7; tbls. 6.

Bureau of Mineral Resources, Geology and Geophysics—Australia, 1957.

Lexicon of the Stratigraphy of Tasmania. E. M. SMITH. Pp. 155; fig. 1. Index, description and distribution of the sedimentary strata of Tasmania.

The Australian Mineral Industry—Quarterly Review and Quarterly Statistics. Vol. 10, No. 1. Pp. 15; tbls. 16. Price, 3 sh. *Production statistics, discussion of domestic tin deficiency.*

Rept. 26. Eruptive Activity and Associated Phenomena, Langila Volcano, New Britain. G. A. TAYLOR, J. G. BEST, and M. A. REYNOLDS. Pp. 49; pls. 13. *Description of volcanic activity on the island of New Britain 1952–56. Discussion of type and character of flows and ejactamenta, possible causes of eruption.*

British Columbia Department of Mines—Victoria, 1957.

Bull. 38. Geology of the Antler Creek Area Cariboo District, British Columbia. A. S. BROWN. Pp. 105; pls. 9; figs. 23; tbls. 23. *Areal geology, stratigraphy, structure and economic geology of the area around Barkerville in central British Columbia. Placer gold once an important product.*

Bull. 39. Geology of Lower Jervis Inlet, British Columbia. W. R. BACON. Pp. 49; pls. 8; figs. 7. *Areal and economic geology of granitic terrain of a part of the Coast Mountains northwest of Vancouver.*

Bull. 40. Calcareous Deposits of Southwestern British Columbia. W. H. MATHEWS and J. W. MCCAMMON. Pp. 103; figs. 16. *Distribution and description of known and potential commercial calcareous deposits in southwestern British Columbia.*

University of California Publications in Geological Sciences—Berkeley and Los Angeles, 1957.

Vol. 32, No. 3. Lower Tertiary Foraminifera from Contra Costa County California. B. Y. SMITH. Pp. 115; pls. 16; figs. 5. Price, $2.50. *Description of 181 species of Foraminifera from the Lower Tertiary.*

Vol. 32, No. 4. Propylitization of Tertiary Volcanic Rocks Near Ebbetts Pass, Alpine County, California. G. WILSHIRE. Pp. 29; pls. 2; figs. 3; tbls. 2. Price, 75 cents. *Heating of groundwater by intrusive magmas suggested as principle cause of propylitization.*

Illinois Geological Survey—Urbana, 1957.

Circ. 226. Gypsum and Anhydrite in Illinois. D. B. SAXEY and J. E. LAMAR. Pp. 26; figs. 7; tbl. 1. *Gypsum and anhydrite restricted to the St. Louis limestone formation in southern Illinois. Found at minimum depth of 470 feet. Further drilling may find commercial supplies.*

Circ. 227. Weathering of Illinois Coals During Storage. H. W. JACKMAN, R. L. EISSLER, and F. H. REED. Pp. 22; figs. 5; tbls. 18.

Circ. 228. Strippable Coal Reserves of Illinois. Pt. 1.—Gallatin, Hardin, Johnson, Pope, Saline, and Williamson Counties. W. H. SMITH. Pp. 39; pls. 4; figs. 2; tbls. 10. *Maps, scale 1 inch : 3 miles, show outcrops, mineral-out areas, thickness of coal, and isopach lines dividing overburden into thickness categories of 0–50, 50–100, and 100–150 feet. Coal reserves in each overburden category estimated by township.*

Circ. 229. Graphic Analyses of Oil Well Drilling and Production, 1937–1955. L. L. WHITING and M. O. OROS. Pp. 28; figs. 13; tbls. 4.

Circ. 230. Subsurface Dolomite and Limestone Resources of Grundy and Kendall Counties. M. E. OSTROM. Pp. 25; figs. 7; tbl. 1. *Seven dolomite or limestone formations ranging up to 379 feet thick contain significant thicknesses of carbonate rocks. Several areas are underlain by such rocks at shallow depths.*

Circ. 231. Refraction Seismic Investigations Rosiclare Fluorspar District, Illinois. Pt. 1.—Goose Creek Area. R. B. JOHNSON. Pp. 15; figs. 7. *Seismic data, obtained by standard reversed-profile refraction shooting, have been correlated with subsurface geologic data obtained from core drilling.*

Circ. 232. Groundwater Geology in Western Illinois, South [illegible]art. A Preliminary Geologic Report. R. E. BERGSTROM and A. J. ZEIZEL. Pp. 28; figs. 7; tbl. 1.

Circ. 233. Pottery Clay Resources of Illinois. E. C. JONAS. Pp. 8; figs. 2. *Location of Clay deposits, simple tests for distinguishing pottery clay, source rocks.*

Circ. 234. Microscopy of the Resin Rodlets of Illinois Coal. R. M. KOSANKE and J. A. HARRISON. Pp. 14; pls. 4. *Examination in transmitted and reflected light has failed to identify positively the origin of the resin rodlets.*

Circ. 235. Spectrochemical Determination of Copper, Nickel, and Vanadium in Crude Petroleum. KOZO NAGASHIMA and J. S. MACHIN. Pp. 10; tbls. 4. *Description of analytical procedure. Precision of 1 ppm in the range 1–10 ppm.*

Circ. 236. Fluid Flow in Petroleum Reservoirs. I.—The Kozeny Paradox. WALTER ROSE. Pp. 8; figs. 2. *Apparent contradiction of the Kozeny fluid flow equation.*

Circ. 237. Studies of Waterflood Performance. III.—Use of Network Models. WALTER ROSE. Pp. 31; figs. 11; tbls. 4. *New computer methods allow study of characteristics of larger and more complex three-dimensional networks.*

Circ. 238. Mineral Production in Illinois in 1956. W. L. BUSCH and W. H. VOSKUIL. Pp. 36; figs. 6; tbls. 17.

Circ. 239. Use of Trace Metals to Identify Illinois Crude Oils. P. A. WITHERSPOON and KOZO NAGASHIMA. Pp. 16; figs. 4; tbls. 5. *Trace content of vanadium and nickel found to increase with age but ratio varies only slightly and cannot be used for identification.*

Bull. 82. Geology and Mineral Resources of the Beardstown, Glasford, Havana and Vermont Quadrangles. H. R. WANLESS. Pp. 233; pls. 7; figs. 66; tbls. 6. *Comprehensive report on Paleozoic and Pleistocene stratigraphy, structure and geologic history of coal producing area in west central Illinois.*

Geological Survey of Japan—Hisamoto-chō, Kawasaki-shi, 1956–57.

Tōkyō. Geological map 1 : 500,000.

Hachijōjima. Geological map 1 : 50,000.

Matsuyama. Geological map 1:200,000.

Index to Geological Sheet Maps of Japan.

Geological Survey of Kansas—Lawrence, 1957.

Bull. 127, Pt. 1. Review of Geophysical Activity in Kansas Through 1956. W. W. HAMBLETON and D. F. MERRIAM. Pp. 22; figs. 2; tbls. 1. *Brief review of geophysical activity in Kansas 1937–1957. Bibliography of published work.*

Bull. 128. Oil and Gas Developments in Kansas During 1956. E. D. GOEBEL, A. L. HORNBAKER, P. L. HILPMAN, and D. L. BEENE. Pp. 239; pls. 3; figs. 2; tbls. 66. *Oil production 124,467,713 barrels ($350,998,951). Gas production 525.9 billion cubic feet. 135 new oil fields were discovered, 35 gas fields and 3 oil and gas fields.*

Subsurface Correlation and Stratigraphic Relation of Rocks of Mesozoic Age in Kansas. D. F. MERRIAM. Pp. 25; pls. 3; figs. 10. *Stratigraphy and structure of Triassic, Jurassic and Cretaceous rocks of Kansas. No petroleum production from the Mesozoic.*

Service Geologique de Madagascar—Tananarive, 1955.

Fasc. No. XXI. Ammonites Néocrétacées du Menabe (Madagascar). II. —Les Pachydiscidae. MAURICE COLLIGNON. Pp. 91; pls. 28. *Occurrence and description of the ammonite genus Pachydiscidae in Madagascar. In French.*

Fasc. No. XXII. Ammonites Néocrétacées du Menabe (Madagascar). III. —Les Kossmaticeratidae. MAURICE COLLIGNON. Pp. 51; pls. 12. *Description of the ammonite genus Kossmaticeratidae in Madagascar. In French.*

Geological Survey of Missouri—Rolla, 1957.

Circ. 14. Exploration and Development of the Sedimentary Iron Ores of Missouri. W. C. HAYES. Pp. 33; figs. 3; tbls. 8. *Distribution, mineralogy and character of deposits. Residual "brown ores" in Missouri.*

Rept. of Investigations 22. Geology of the Bowling Green Quadrangle, Missouri. T. J. LASWELL. Pp. 61; pl. 1; figs. 4. *Areal geology, stratigraphy and structure of the Ordovician to Pennsylvanian rocks of northeast Missouri. Limestone, shale, dolomite, sand, gravel and water are the only economic products.*

State of New York Department of Conservation, Water Power and Control Commission—Albany, 1956–57.

Bull. GW-36. Saline Waters in New York State. Long Island, Staten Island and Manhattan. N. J. LUSCZYNSKI and J. J. GERAGHTY. **Upstate New York.** E. S. ASSELSTINE and I. G. GROSSMAN. Pp. 8; fig. 1; tbls. 4. *Distribution of waters within greater than 1,000 ppm salinity and possible utilization after demineralization.*

Bull. GW-37. The Ground Water Resources of Putnam County, New York. I. G. GROSSMAN. Pp. 77; pls. 2; figs. 7; tbls. 20. *Survey of water resources in southeastern New York State. Present yield of 500,000 gallons a day is substantially below possible output.*

Ontario Department of Mines—Toronto, 1957.

Sixty-Fifth Annual Rept. Vol. LXV, Pt. 2, 1956. Mining Operations in 1955. D. J. FIELD. Pp. 162. *Mining activity in Ontario during 1956.*

Map No. 1956-4. Clarendon-Dalhousie-Darling Area. Scale, 1:63,360. *Precambrian metamorphic and igneous terrain southwest of Armprior.*

Geological Survey of West Virginia—Morgantown, 1957.

Rept. of Investigations 16. Sandstones of West Virginia. T. ARKLE, JR., and R. G. HUNTER. Pp. 58; figs. 23; tbls. 9. *Distribution and description of sandstone occurrences. Utilization as building material, refractories, for glass making, filtration, foundry sands, etc.*

State Park Series Bull. 5. Geology of the Coopers Rock State Forest and Mont Chateau State Park, West Virginia. C. E. HARE. Pp. 26; pls. 14; figs. 4. *Brief descriptions of the Mississippian and Pennsylvanian sediments of northern West Virginia.*

Geologic Map of the Ohio River Valley in West Virginia. A. L. CROSS and M. P. SCHEMEL. *Map 1, scale 1:250,000. Map 2, in 3 sheets, Northern, Central, and Southern sections, scale 1:125,000, showing mineral and other resources.*

Univerzitet U Beogradu—Beograd, 1955–56.

Geologija i Metalogeneza Alovno-Cinkovog Rudišta Šuplje Stijne (Crna Gora). SLOBODAN JANKOVIĆ. Pp. 105; pls. 13; figs. 55; tbl. 1. *Excellent photographs of microscopic ore structures. German abstract. Geologic map, scale 250 meters: ¾ inch.*

SV. 3. Transactions of the Geological and Mining Faculties, University of Beograd 1955. Pp. 116; pls. 2; figs. 43; tbls. 2. *English, German, or French abstracts; 12 articles.*

SV. 4. Transactions of the Geological and Mining Faculties, University of Beograd 1956. Pp. 197; pl. 1; figs. 131; tbls. 45. *21 of the 23 articles have English, German, or French abstracts.*

U. S. Geological Survey—Washington, D. C., 1957.

Bull. 1046-C. Uranium-Bearing Minerals in Placer Deposits of the Red River Valley, Idaho County, Idaho. F. C. ARMSTRONG and P. L. WEIS. Pp. 10; pl. 1; fig. 1, tbls. 3. Price, 30 cents. *Brannerite, euxenite, davidite, betafite and samarskite occur in the placer gravels and are probably derived from pegmatites.*

Bull. 1046-D. Uranium Resources of the San Rafael District Emery County, Utah—a Regional Synthesis. H. S. JOHNSON, JR. Pp. 17; pl. 1; figs. 2; tbl. 1. Price, 40 cents. *Estimated 90 percent of potential reserves expected in deposits larger than 100,000 tons, and 40 percent expected at depths of less than 1,000 feet. Map, scale 6 miles : 1 inch.*

Bull. 1050. The Spotted Horse Coalfield, Sheridan and Campbell Counties, Wyoming. W. W. OLIVE. Pp. 83; pls. 13; fig. 1; tbls. 3. *Description of the Tertiary stratigraphy and reserves of coal in the Wasatch and Fort Union formations. Two geologic maps, scale 1:63,360.*

Bull. 1063-A. Stratigraphic and Structural Controls of Uranium Deposits on Long Mountain, South Dakota. W. A. BRADDOCK. Pp. 11; pls. 4; figs. 4. Price, $1.00. *Evidence suggests northeastward-trending fault zone as primary control. Sedimentary structures in two sandstone units containing ore less important. Geologic map, scale 500 ft : 1 inch.*

Bull. 1066-B. Geophysical Abstracts 169 April–June 1957. M. C. RABBITT, D. B. VITALIANO, S. T. VESSELOWSKY, and others. Pp. 190. Price, 25 cents.

Bull. 1071-A. The Gold Pan as a Quantitative Geologic Tool. P. K. THEOBALD, JR. Pp. 54; figs. 4; tbls. 8. Price, 25 cents. *Recovery of minerals is related to grain size, grain shape, specific gravity, and amount of clay or silt present.*

Water-Supply Paper 1305. Compilation of Records of Surface Waters of the United States through September 1950. Pt. 3-a. Ohio River Basin Except Cumberland and Tennessee River Basins. Pp. 643; pl. 1; figs. 2. Price, $2.25. *Streamflow and reservoir data.*

Water-Supply Paper 1372. Compilation of Records of Quantity and Quality of Surface Waters of Alaska through September 1950. J. V. B. WELLS and S. K. LOVE. Pp. 257; pl. 1; fig. 1. Price, $1.50. *Summary of streamflow and reservoir data for Alaska up to 1950.*

Water-Supply Paper 1413. Geology and Ground-Water Resources of Kitsap County Washington. J. E. SCEVA. Pp. 178; pls. 3; figs. 26; tbls. 7. *Geologic and water table maps, scale 1:48,000.*

Economic Geology
Vol. 52, 1957, pp. 989–990

SCIENTIFIC NOTES AND NEWS

EDWARD H. EAKLAND, JR. and ROBERT W. OSTERSTOCK announce their association as consulting mining geologists at 700 Newhouse Bldg., 10 Exchange Place, Salt Lake City, Utah. Mr. Eakland was formerly associated with Iron and Steel Division, Kaiser Co., Inc., Union Mines Development Co., International Smelting and Refining Co., and the Anaconda Mining Co. as exploration geologist. Mr. Osterstock was employed by the American Metal Co. and the U. S. Geological Survey. (A correction.)

W. S. MCCANN has been appointed by the United Nations, under their Technical Assistance Program, to advise the Venezuelan government on certain aspects of mining development.

WILFRED A. LYONS, formerly geologist for Cia Minera Aguilar, Argentina, has been appointed Resident Geologist in Pulacayo, Bolivia, for Corporacion Minera de Bolivia.

HOLMAN D. PETTIBONE, chairman of the board of the Chicago Title and Trust Co., has been appointed to head a U. S. Government advisory committee to study America's stockpile of minerals, metals and materials.

RICHARD D. ELLETT, geologist with National Lead Co., has been in charge of the company's extensive exploration program for copper within the Northern Territory of Australia.

C. G. B. DU BOIS has returned from the United Kingdom to resume his duties as geologist with the Geological Survey of Uganda.

J. HAYS has resigned his position with the Northern Rhodesian Geological Survey to accept a post with the Australian Federal Government.

J. N. L. MONRO has left the Department of Mines, Malaya, and is now in Auckland, New Zealand.

PHILIP D. WILSON has been elected a vice president of Callahan Zinc-Lead Co.

RICHARD M. FOOSE has been appointed head of the newly formed Earth Sciences Department of Stanford Research Institute's Physical Sciences Div., Menlo Park, Calif. Formerly he was chairman of the Geology Department, at Franklin and Marshall College, Lancaster, Pa.

RENE ENGEL, consulting geologist and geochemist recently moved his petrographic and geochemical laboratory from South Pasadena, Calif, to Wofford Heights, Kern County, Calif., where he now resides.

LYMAN C. HUFF, formerly with the U. S. Geological Survey, Denver, is now associated with the Military Geology Branch, USGS, Washington, D. C.

EUGENE C. ANDERSON, mining engineer, has retired from the New Mexico Bureau of Mines and Mineral Resources and opened a consulting office in Socorro, N. M.

RICHARD C. LUNDIN of the Eagle-Picher Co., has succeeded Douglas Brockie as senior geologist in the Tri-State District.

WILLIAM E. ARNT of the same company has been promoted to senior geologist in the Illinois-Wisconsin area operations and exploration.

ROBERT A. CHADWICK, III, also of Eagle-Picher, who has been working on special projects in the Tri-State field, has taken over additional exploration work for the company.

E. A. HICKOK, ground-water geologist, is now associated with the recently organized firm of Geraghty, Miller and Hickok, consulting ground-water geologists, in New York.

C. L. THORNBURG, mines geologist with the U. S. Smelting, Refining and Mining Co. was awarded a professional degree by the College of Mines, University of Utah, at its commencement ceremonies last June. The awards are made to former graduates who have distinguished themselves in their fields.

THOMAS G. MURDOCK, American Consul and Regional Minerals Officer since 1948 for the U. S. State Dept. in Elizabethville, Belgian Congo, after a visit in the U. S., left on July 30 for Ankara, Turkey, to take up his new post as First Secretary and Regional Minerals Officer at the U. S. Embassy.

JOSEPH C. ARUNDALE succeeds MR. MURDOCK in Elizabethville. Before his appointment to the Foreign Service Mr. Arundale was assistant chief in the branch of construction and chemical materials, USBM, Washington, D. C.

HAYDN H. MURRAY has left the Department of Geology at the University of Indiana and is now working in the Research Division, Georgia Kaolin Co., Elizabeth, N. J.

JAMES G. HENDERSON has been transferred to Grand Junction, Colo., after completing an assignment in Spain for the U. S. Atomic Energy Commission.

EARL F. COOK has been appointed Dean of the University of Idaho, College of Mines, and Director of the Idaho Bureau of Mines and Geology.

E. A. ECKHARDT, geophysicist, has been appointed assistant director of the National Science Foundation for the Division of Mathematics, Physical and Engineering Sciences.

OLIVER C. RALSTON, chief metallurgist of the U. S. Bureau of Mines since 1949, retired recently after serving with the Bureau since 1912.

A. RAYMOND JORDAN, formerly of the Denver Research Institute, was appointed Dean of the graduate school of Colorado School of Mines, effective October 1.

JAMES A. BARR, consulting engineer, left on Sept. 19 for Rome, Italy, on a minerals economic mission for the World Bank.

ROYCE A. HARDY, JR., of Henderson, Nev., has been named Assistant Secretary of the Interior for Mineral Resources, to replace FELIX WORMSER who resigned June 15.

ALEXANDER SILVERMAN, authority on chemistry of glass, has been retained as a special consultant to Foote Mineral Co. to assist in its research into the use of lithium in inorganic chemistry and glass technology.

W. R. LANDWEHR, chief geologist of Western Mining Department of American Smelting and Refining Co., has been made its acting manager at Salt Lake City.

W. T. ROBSON has been appointed general manager of Lake Shores Mines Ltd. A member of the Canadian Institute of Mining and Metallurgy, Mr. Robson was a recipient in 1937 of the Barlow Memorial Prize for his paper on "Lake Shore Geology."

THEODORE W. BECKER, geologist for Mining Division of Union Pacific Railroad, died at the age of 37 in a helicopter crash at Rawlins, Wyoming, on August 16, 1957.

THE INDEX TO THIS VOLUME HAS BEEN REMOVED FROM THIS POSITION AND PLACED AT THE BEGINNING OF THE FILM FOR THE CONVENIENCE OF READERS

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E. A. ECKHARDT, geophysicist, has been appointed assistant director of the National Science Foundation for the Division of Mathematics, Physical and Engineering Sciences.

OLIVER C. RALSTON, chief metallurgist of the U. S. Bureau of Mines since 1949, retired recently after serving with the Bureau since 1912.

A. RAYMOND JORDAN, formerly of the Denver Research Institute, was appointed Dean of the graduate school of Colorado School of Mines, effective October 1.

JAMES A. BARR, consulting engineer, left on Sept. 19 for Rome, Italy, on a minerals economic mission for the World Bank.

ROYCE A. HARDY, JR., of Henderson, Nev., has been named Assistant Secretary of the Interior for Mineral Resources, to replace FELIX WORMSER who resigned June 15.

ALEXANDER SILVERMAN, authority on chemistry of glass, has been retained as a special consultant to Foote Mineral Co. to assist in its research into the use of lithium in inorganic chemistry and glass technology.

W. R. LANDWEHR, chief geologist of Western Mining Department of American Smelting and Refining Co., has been made its acting manager at Salt Lake City.

W. T. ROBSON has been appointed general manager of Lake Shores Mines Ltd. A member of the Canadian Institute of Mining and Metallurgy, Mr. Robson was a recipient in 1937 of the Barlow Memorial Prize for his paper on "Lake Shore Geology."

THEODORE W. BECKER, geologist for Mining Division of Union Pacific Railroad, died at the age of 37 in a helicopter crash at Rawlins, Wyoming, on August 16, 1957.

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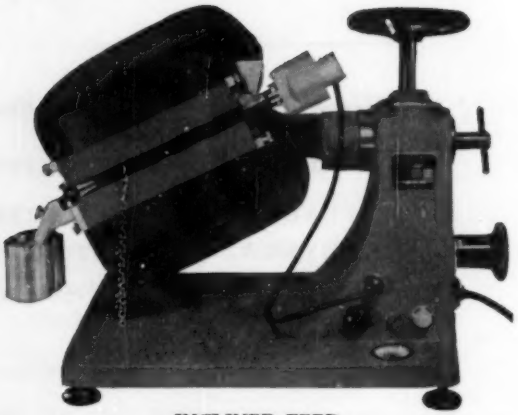

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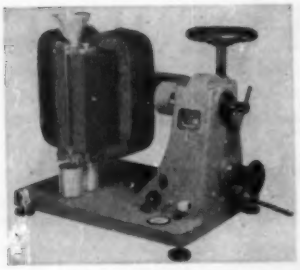

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